NEAR NET SHAPE MANUFACTURE OF CMC COMPONENTS

W. Krenkel, N. Lützenburger

Institute of Structures and Design, German Aerospace Center (DLR),
Pfaffenwaldring 38-40, 70569 Stuttgart, Germany.

Abstract

Dimensional stability and reproducibility of the different processing steps for ceramic matrix composites (CMC) is one of the major demands when manufacturing complex structures. Depending on size, shape and required accuracy, the machining of the finished ceramic part can amount to an essential share of the overall production costs. Generally, the lower the total shrinkage during fabrication, the lower the tooling and machining effort. This paper deals with a processing technique which is based on the infiltration of a fluid phase into a porous fibre preform, showing extremely low dimensional changes. The macroscopic shrinkage only occurs in one direction and amounts to less than 7 %. Due to this high dimensional stability during the three step process, complex ceramic matrix composite (CMC) structures can be manufactured cost efficiently.

1.   Introduction

CMC materials can be manufactured using processing techniques which are based on the infiltration of reactive fluid phases into porous carbon or ceramic fibre preforms. These reactive fluids are normally preceramic polymers (e.g. polycarbosilanes) or molten metals which replace the initial pore volume of the preform. The subsequent reaction of the infiltrant with the fibre structure normally shows dimensional changes due to density and mass changes within the matrix. In cases where the preform material remains chemically unaltered and macroscopic changes of the composite are constrained by the rigidity of the fibre, several infiltration steps are necessary in order to achieve a dense or nearly dense material.

The manufacture of CMC components by the pyrolysis of preceramic polymers is known as the liquid polymer infiltration (LPI) process [1]. In order to obtain a dense matrix within the herewith manufactured composite, multiple reinfiltration and thus many process steps are necessary. The greater the fibre volume fraction of the composite and the higher the ceramic yield of the precursor (or rather, the smaller the jump in density from Si-polymer to ceramic), the lower the number of reinfiltration steps.

Under the assumption that there is no macroscopical change in the geometry of the preform during pyrolysis and that the resulting porosity after each impregnation step remains accessible (i.e. there is no closed porosity), the residual porosity, e'_n, in relationship to the number of infiltration steps, n, can be calculated. With a known ceramic yield, M, afer polymer pyrolysis and the given density ratio, R, the following equation is generally valid for open porosity:

$$e'_n = (1 - \phi_f).(1 - V)^n \quad \text{where} \quad V = \frac{M}{R} \tag{1}$$

e'_n open porosity after pyrolysis

ϕ_f fibre volume fraction

M ceramic yield of the matrix $\dfrac{m_2}{m_1}$

R density ratio of the matrix $\dfrac{\rho_2}{\rho_1}$

As demonstrated with an exemplary polymer ($\rho = 1.2$ g/cm³) in Figure 1, in order to obtain a ceramic matrix ($\rho = 3.0$ g/cm³) with a technically relevant residual porosity of 10 % maximum, somewhere between three and seven infiltration steps are necessary.
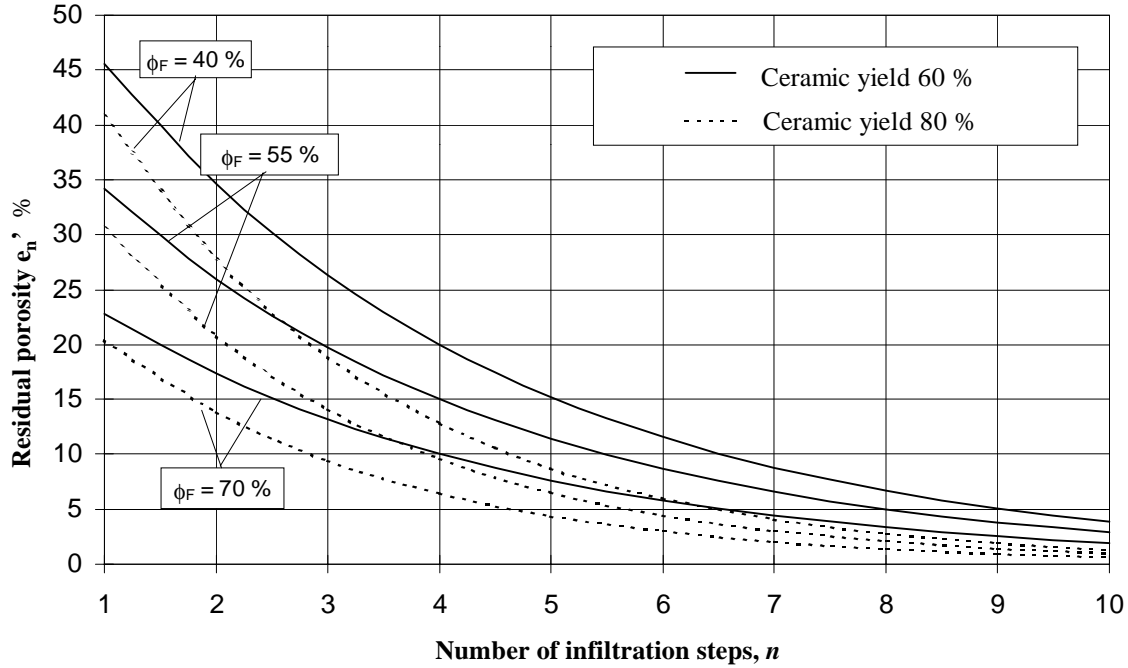

Fig. 1:   *Residual porosity of CMC materials manufactured using the LPI process, in relationship to the number of infiltration steps, the ceramic yield of the precursor and the fibre volume fraction.*

The contraction of the matrix during ceramming can be hindered though the addition of passive (e.g. SiC) or reactive (metallic) powder fillers, which in turn results in a distinct reduction of the number of necessary reinfiltration steps. This, however, requires a special impregnation technique for the fibre bundles, as otherwise there is a danger of the powder additives being sifted out during the green body fabrication.

To overcome this technological restriction, an alternative CMC process based on the infiltration of a metal melt as the liquid phase has been developed. Using molten silicon, porous carbon / carbon (C/C) preforms can be infiltrated without pressure due to the high capillarity of small translaminar cracks within the preform and due to the low wetting angle and high surface tension of the molten silicon. Multidimensional carbon fibre reinforcements remain more or less unaffected during the siliconizing step and lead to composites consisting of load bearing carbon fibres and matrices of silicon carbide, carbon and some free silicon [2, 3]. If an unconstrained flow of liquid silicon into the pore space of the preform can be guaranteed, only one infiltration is necessary despite high volumetric change of the matrix during the formation of silicon carbide. This liquid silicon infiltration (LSI) process represents the basis of a new near net shape manufacture of CMC components.

2.   Theoretical aspects

The stoichiometrical conversion of molten silicon with solid carbon occurs following the equimolar reaction:

$$1 \text{ mol Si}_l + 1 \text{ mol C}_s \rightarrow 1 \text{ mol SiC}_s \qquad \Delta H = -68 \text{ kJ/mol} \qquad (2)$$

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). Silicon carbide therefore consists of approx. 70 wt.% silicon and 30 wt.% carbon. The formation of SiC is, with a reaction enthalpy of -68 kJ/mol, highly exothermic, so that by the conversion of small graphite samples a violent thermal development with a sharp rise in temperature of several hundred degrees is observed.

The aim of the LSI process is to convert the whole or at least a greater majority of the molten silicon through the reaction with carbon to SiC. Through investigations [4] it is known that liquid silicon reacts swiftly with graphitic carbon to form solid SiC on its surface. The primary reaction occurs within a few seconds when the melt seeps in-plane through the graphite layers, which leads to a splitting of numerous individual layers: A secondary, slower process follows with reaction perpendicular to the layers. A dense, pore-free silicon carbide is the resulting reaction product.

In contrast to graphite, the conversion reaction within irregular amorphous carbons is slower. The reaction kinetics for the conversion of carbon to SiC is, however, predominantly dependent on the microstructure, or rather the microporosity, than the degree of graphitization. A fast reaction can occur only under the condition of accessible pores and large surface area.

The quantative conversion of carbon and silicon to silicon carbide in a closed system leads theoretically to a reduction in volume, as the molar volume of silicon carbide is less than the sum of the respective molar volumes of the reactants, Si and C (Table 1).

Table 1:   Density, mass and molar volume of various modifications of carbon in comparison to silicon and silicon carbide.

		Silicon	Graphite	Amorphous carbon	SiC
Density ρ	g/cm³	2,53 (1420°C)	2,26	1,84	3,22
Molar mass M	g/mol	28,09	12,01	12,01	40,10
Molar volume V	cm³/mol	11,11	5,31	6,53	12,45

If the infiltration of silicon in the C/C preform occurs within a communicating sytem, in which the infiltrated silicon remains in contact with the melt, then porosity originating through the formation of SiC can be filled with silicon. This can only occur under the condition that during siliconization, the geometrical volume of the C/C laminate remains constant and hence the succesive flow of silicon in the resulting pores is possible.

The conversion of graphitic carbon to silicon carbide results in a theoretical volume increase of 135 %. For amorphous carbon, with a density of 1.84 g/cm³, the theoretical volumetric expansion is still 91 %. Through the larger molar volume of silicon carbide in contrast to the reactant carbon, there is a principle tendency, with increasing reaction times, that canals and pores close completely.

Elementary silicon possess several characteristics in contrast to most other metals:
- anomaly with phase transition (increase in density of approx. 8 %)

- extremely low coefficient of expansion (4.1 x 10^{-6} 1/K)
- highest enthalpy of liquefication of all metals (50 kJ/mol)

The anomaly of silicon means that a volume expansion during solidification of the molten silicon (ca. 1420 °C) occurs and the density of the solid (2.34 g/cm³) is lower than the melt (2.53 g/cm³). For this reason there is a danger by high residual silicon contents, particularly during cooling, that due to the released enthalpy and the volume increase the C/C-SiC laminate can be destroyed.

In order to successfully siliconize, an exact silicon dosage is necessary to ensure a complete filling of the C/C material on one hand, and to avoid, on the other hand, the danger of component destruction through excessive silicon dosage.

On account of these physical circumstances, the near net manufacture of CMC components is only achievable if a rigid carbon fibre body is used which allows a microscopical volume change within the matrix with negligible macroscopic changes in laminate geometry. This criterion of minimum shape change includes both the silicon infiltration and its reaction, as well as the preceding pyrolysis.

The solid phase pyrolysis of a carbonaceous precursor to an amorphous carbon matrix is coupled with a considerable contraction. This is caused on one hand through the mass loss arising through the formation of decomposition products, on the other hand, through the increase in density of approx. 1.2 g/cm³ in polymeric state to 1.8 g/cm³ after pyrolysis.

In the LSI process, the conversion of the carbon precursor occurs, due to economical consideration, through a one step pyrolysis so that a repeated filling of the matrix is not possible. For these reasons, resin systems with a high yield in carbon which also limit the volume shrinkage are necessary. By introducing thermally stable fibres, the isotropic shrinkage of the matrix can be controlled to such a limit that the macroscopical volume change within the composite is very low. Shrinkage then leads merely to porosity as well as matrix cracks.

With the aim of manufacturing components with as low as possible shrinkage, composite development is focused on high fibre contents, high carbonaceous precursors and multidirectional fibre structures.

3.   Thermal behaviour of the raw materials during pyrolysis

In the first step of the LSI process, carbon fibres and precursors are processed to form a homogeneous and dense carbon fibre reinforced plastic (CFRP) component. Subsequently, the CFRP composites are pyrolysed under inert atmosphere (N_2) at temperatures of between 900 °C and 1650 °C to convert the polymer matrix to amorphous carbon.

3.1   Polymer precursor
Neat resin samples from the precursor XP-60 of various sizes were submitted to parameter studies using thermal analysis. The average mass losses from XP-60 at 900 °C and at 1550 °C lie by 36 % and 39 %, respectively. Thus, at pyrolysis temperatures of 900 °C, the conversion of the precursor to carbon is over 90 % complete.

In order to determine changes in geometry during the pyrolysis, neat resin samples were investigated at temperatures of up to 1500 °C in argon in a dilatometer (Netsch 402 E). In principle, polymer non-reinforced precursors shrink isotropically, by which the extent of volume contraction is dependent upon the mass loss of the carbonized polymer. XP-60 shows in all three spacial axes a more or less equal change in length of approx. 26 % at 900 °C, whereby a volumetric contraction of ca. 60 % within the matrix during pyrolysis occurs.

If the neat resin (*NR*) has a mass ratio of :

$$M = 1 + \left(\frac{\Delta m}{m} \right)_{NR} \qquad (3)$$

a density ratio of:

$$R = 1 + \left(\frac{\Delta \rho}{\rho} \right)_{NR} \qquad (4)$$

and a thickness ratio (under the assumption of isotropic behaviour):

$$D = 1 + \left(\frac{\Delta d}{d} \right)_{NR} = \sqrt[3]{\frac{M}{R}} \qquad (5)$$

then the matrix constants summarized in Table 2 result.

Table 2: Mass and geometry balance for neat XP-60 after pyrolysis at 900 °C.

Mass		Density		Volume		Thickness	
$\left(\frac{\Delta m}{m} \right)_{NR}$	M	$\left(\frac{\Delta \rho}{\rho} \right)_{NR}$	R	$\left(\frac{\Delta V}{V} \right)_{NR}$	V	$\left(\frac{\Delta d}{d} \right)_{NR}$	D
-36 %	0.64	+61.4 %	1.614	-60.35 %	0.396	-26.5 %	0.735

Whilst mass, thickness and volume decrease, the density of the precursor increases by approx. 61 %. In a non-reinforced state, these high volume changes result in an inhomogeneous body interspersed with cracks.

3.2 Investigations on the thermal stability of carbon fibres

The height of thermal treatment during fabrication of carbon fibres determines essentially the carbon content and properties of PAN (polyacrylonitrile) or pitch derived fibres. Whereas high tenacity (HT) or intermediate modulus (IM) fibres are carbonized at temperatures of up to 1500 °C, by the manufacture of so-called high modulus (HM) and ultra high modulus (UHM) fibres is completed with a graphitizing step at temperatures of up to 3000 °C in order to achieve carbon contents of over 99 %.

Carbon fibres are manufactured with a sizing agent (approx. 1-1.5 % share of the fibre mass) in order to protect the fibre from abrasion and improve its handling. The typical sizing agent, epoxy resin, optimized for carbon fibres regarding their main application within fibre reinforced plastics, was removed before the thermogravimetrical analysis in order to better compare results. Thus all investigated fibres were desized at 600 °C for one hour in a nitrogen atmosphere.

Thermal analysis conducted on the carbon fibres showed that there are large fibre specific differences concerning both the thermal stability barrier and mass change (Fig. 2).

High tenacity fibres show a mass loss of between 2 % (Hysol XA-S) and 6.3 % (Torayca T700), which starts at 800 °C. IM-fibres (Torayca T800 and T1000) are with mass losses of 2.7 to 3.0 % slightly more thermally stable, whilst all investigated high and ultra high modulus fibres showed practically no change in mass. As a compromise between thermal stability and economy, further investigations were conducted with high tenacity fibres (AKZO HTA).
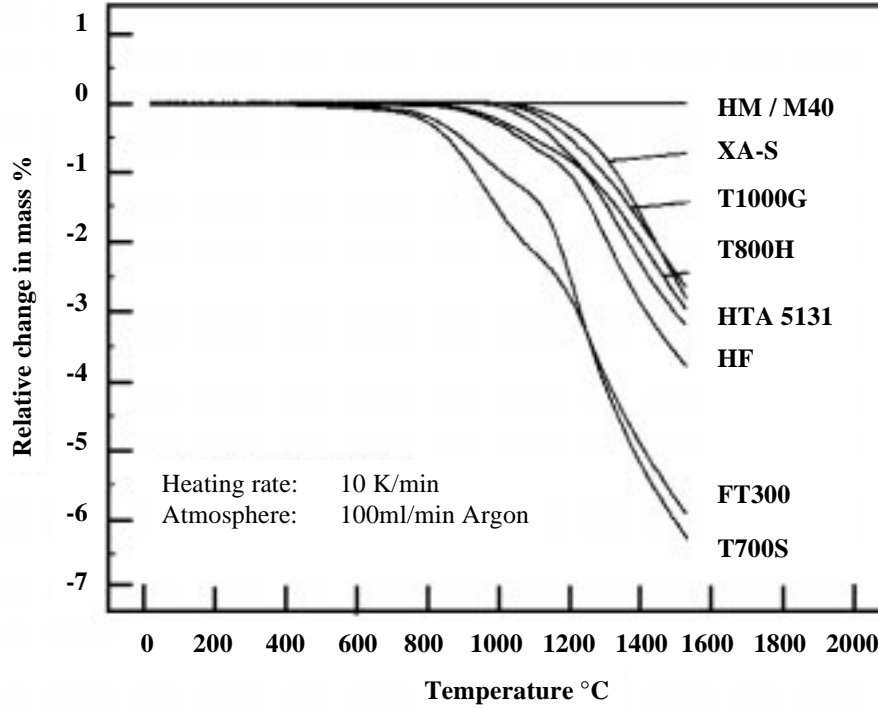
Fig. 2: Thermal investigations on various carbon fibres.

4.   Geometry and mass balance by the manufacture of C/C-SiC components.

Two dimensional reinforcements of woven carbon fabrics have been used to investigate the manufacture of nearly net shaped CMC components by applying the Liquid Silicon Infiltration (LSI) process. Under the assumption that dimensional change is prevented by the thermally stable fibres in plane, a macroscopical change in geometry for two dimensional laminates occurs primarily in the thickness, i.e. perpendicular to the fibres. This change in geometry is strongly dependent on interfacial bond strength between the fibre and the matrix and can not be directly derived from the dimensional changes of the individual components.

For the extreme case of high fibre/matrix bond strengths, the laminate shrinks theoretically proportionally to the matrix contraction. The change of thickness arising through pyrolysis can then be derived as:

$$\left(\frac{\Delta d}{d}\right)_{C/C} = (D-1)(1-\phi_{f_{CFRP}}) \tag{6}$$

D thickness ratio of the precursor during pyrolysis
$\phi_{f_{CFRP}}$ fibre volume fraction in the CFRP state

The overall change in mass of the matrix during pyrolysis is an order of magnitude higher than that of the carbon fibres. Thus, for a first approximation, the influence of the size as well as the fibres can be neglected. Under this assumption, equation 7 is valid for changes in mass arising through pyrolysis.

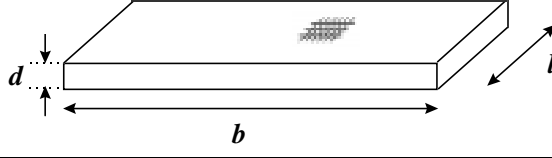$$\left(\frac{\Delta m}{m}\right)_{C/C} = (M-1)(1-\Psi_{f_{CFRP}}) \tag{7}$$

M   mass ratio of the precursor during pyrolysis
$\Psi_{f_{CFRP}}$ fibre mass fraction in the CFRP state

4.1 Experimental results for 2D-laminates

Standard laminates (300 x 300 x 10 mm³) manufactured with plain weave high tenacity carbon fibre fabrics (AKZO HTA) and a thermosetting resin (XP-60) using resin transfer moulding in the first step of the LSI-process were chosen for demonstrating near net shape CMC fabrication (Table 3).

Table 3: Characteristics of the CFRP laminates under investigation.

Geometry		d = 10 mm b = 300 mm l = 300 mm
Matrix	XP-60	
Fibre/fabric	HTA, plain weave	
Lay-up	0°/90°, 44 plies	
CFRP process	Resin Transfer Moulding (RTM)	
Fibre content	approx. 60 %	
Density	1.49 g/cm³	
Open porosity	< 1 %	

Within the second step, the CFRP composites are pyrolysed under inert atmosphere (N_2) at elevated temperatures to convert the polymer matrix to amorphous carbon. To achieve a carbon fibre reinforced carbon material- C/C- in one processing step, the pyrolysis must be conducted without inducing stresses that can lead to defects in the microstructure of the composite, and only precursors of high carbon yield can be used. In the case of two directional reinforcements, the resulting C/C composite material has an interconnecting pore structure which can be described as a translaminar crack pattern with an open porosity of about 20 %.

In addition to the process related matrix cracks, a microcrack pattern arises through the shrinkage impediment which is distinctly influenced by the fibre architecture, the processing parameters and the fibre/matrix interface. This microcrack system is also influenced by component size.

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 so that liquid silicon can penetrate the porous C/C phase, supported by the specific properties of silicon, e.g. wettability of carbon, high surface tension and low viscosity. Generally, the molten silicon penetrates preferably along the fibre direction. 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 (SiC). 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 composite material. Table 4 summarizes the conditions of the individual process steps.

Table 4: Summary of process conditions for each individual step.

	Cure	Postcure	Pyrolysis	Siliconization
Temperature	208 °C	240 °C	900 °C / 1650 °C	> 1420 °C
Atmosphere	N_2	air	N_2 . / vacuum	vacuum
Pressure	> 20 bar	1 bar	1 bar / < 0.001 bar	< 0.001 bar
Material	CFRP	CFRP	C/C	C/C-SiC

In order to evaluate the volumetric change within the laminate during processing, the dimensions (thickness, length and breadth) of each manufactured plate were measured in 20 mm steps using a digital micrometer (Mitutoyo MDC-25L) with an accuracy of 0.001 mm after each process step. In addition, mass changes were determined by weighing the plates before and after each process step using weighing scales with an accuracy of 0.01 g.
A summary of the results is given in Table 5.

Table 5: Dimensional and mass changes occurring within 10 mm 2D-laminates (HTA fibres, XP-60) during the LSI process in relationship to the previous material state.

		CFRP cured	CFRP postcured	C/C pyrolysed at 900 °C	C/C pyrolysed at 1650 °C	C/C-SiC siliconized
$\frac{\Delta d}{d}$	%	-	0	-4.4	-1.3	0
$\frac{\Delta b}{b}$	%	-	0	0	-0.25	0
$\frac{\Delta l}{l}$	%	-	0	0	-0.25	0
$\frac{\Delta V}{V}$	%	-	0	-4.4	-1.74	0
$\frac{\Delta m}{m}$	%	-	-1.1	-11.6	-3.1	+44.0

The investigations show that postcuring incurs a negligible mass loss of approx. 1.1 % with no volumetric change.

Mass loss during pyrolysis ranges from 11.6 % (T = 900 °C) to 14.3 % (T = 1650 °C). This is accompanied by a macroscopical dimensional change, which due to the shrinkage impediment of the fibres only occurs transverse to the fabrics. In the case of the 900 °C pyrolysis the laminate thickness shrinks by approx. 4.4 %. The pyrolysis step at 1650 °C under vacuum results in an additional volumetric contraction of 1.74 %. Here, the main geometrical change also occurs in the direction of the laminate thickness. Minor changes (-0.25 %) occur in breadth and length. During siliconization, mass increases by 44 % without any essential change in shape and geometry.

In total, the anisotropic characteristics of the laminates result in dimensional changes over the whole process of less than -7 %. This shrinkage occurs mainly in one direction, namely perpendicular to the fibre orientation. Summarized, 2D-CMC composites manufactured via the LSI-process show extremely low dimensional changes and macroscopical shrinkage only occurs during the pyrolysis step.
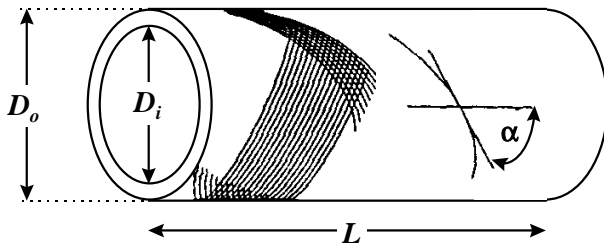
4.2   Experimental results from thin walled tubes

In addition to the laminates, tubes with wall thickness of 3 mm and a length of 250 mm were evaluated during the stages of the LSI manufacturing process. The studied geometries and component details are given in Table 6. In order to determine the influence of fibre orientation, tubes of 0°/90° as well as ± 45° fibre orientation were manufactured using resin transfer moulding techniques and winding plain weave HTA fabric tapes. Impregnation took place in a heatable two chamber mould at 170 °C, with a subsequent cure at 208 °C over ten hours. The tubes were then postcured at 240 °C in air, before the pyrolysis at 900 °C.

In contrast to the 0°/90° flat laminates where the matrix adopts a crack pattern in both circumferential and radial directions due to the fibre impediment, the radial shrinkage is hindered here by the geometrical contour of the tubes resulting in additional compression stresses in the hoop direction. To maintain the cylindrical shape, all tubes were pyrolysed with graphite cores. The tubes were then siliconized at 1650 °C under vacuum.

Table 6: Processing parameters for thin walled tubes

Dimensions	$D_o = 28.5$ mm $D_i = 25.5$ mm $L = 250$ mm
Fibre content	58 Vol. %
Fibre	HTA
Fabric	plain weave
Matrix	XP-60
CFRP process	Resin Transfer Moulding (RTM)
Pyrolysis	900 °C / N_2

The tubes were measured before and after each process step. In addition to diameter measurements, mass changes and porosity evaluation was conducted. Inner diameter (D_i) measurements were conducted in 20° steps at both ends of the tube. The outer diameter (D_o) measurements were taken at intervals of 30 mm along the length of the tube, as well as in 20° steps around the circumference. A digital caliper (Mitutoyo CD-15C) with an accuracy of 0.01 mm was used to ascertain the dimensions of the tubes.

The investigations show that as for the laminates, the postcure has no volumetric effect on the tubes and results in a mass loss of approximately 0.5 %. As such, these results have been omitted from the summary of dimensional and mass changes given in Table 7.

Table 7: Dimensional and mass changes occurring within 3 mm thin walled tubes (HTA fibres, XP-60) during the LSI process in relationship to the previous material state.

Fibre orientation	C/C (900 °C)				C/C-SiC			
	$\dfrac{\Delta m}{m}$	$\dfrac{\Delta D_o}{D_o}$	$\dfrac{\Delta D_i}{D_i}$	e'	$\dfrac{\Delta m}{m}$	$\dfrac{\Delta D_o}{D_o}$	$\dfrac{\Delta D_i}{D_i}$	e'
α	%	%	%	%	%	%	%	%
0°/90°	-12.0	-0.2	+0.25	19.2	+42.0	-0.22	-0.6	4.7
$\pm\,45°$	-12.0	-0.4	-0.1	18.7	+42.0	-0.25	-0.6	3.5

From the results given in the table above it can be clearly seen that the geometrical changes throughout the LSI process are extremely low, amounting to a total of less than -1 %, for thin walled tubes. The open porosity, e', for the $\pm$ 45° tubes is slightly lower than for the 0°/90° tubes.

The greatest dimensional changes and deviation in behaviour of the differing fibre oriented tubes occur during the pyrolysis at 900 °C in nitrogen atmosphere. Here, the $\pm$ 45° tubes show a decrease in both outer diameter (D_o, given as a mean value of both circumferential and longitudinal measurements) and, to a lesser extent, inner diameter (D_i) of -0.4 % and -0.1 %,

respectively. In contrast, the 0°/90° tubes show a smaller decrease (-0.2 %) in the outer diameter and an increase (+0.25 %) in the inner diameter, by identical mass losses. This is the equivalent of a reduction in wall thickness of 3 % and 4 % for ± 45° and 0°/90° tubes, respectively. In general, the higher the circumferential reinforcement, i.e. the higher the fibre orientation, the higher the radial shrinkage impediment, which in turn may cause local delamination.

6.   Conclusions

The liquid silicon infiltration process described in this paper can be successfully used to manufacture near net shaped components. Investigations on the basis of 2D-laminates show extremely low contraction. This shrinkage occurs in one direction only, namely perpendicular to the fibre plies within the laminate thickness. The main geometrical changes occur during the pyrolysis at 900 °C and shape stability is achieved after this step. Despite the anomaly of silicon and the distinct differences in molar volume of the reactants, no volumetric change is observed through siliconization. A similar dimensional stability is observed for thin walled tubes manufactured by the LSI-process. Inner stresses result here due to the anisotropic shrink behaviour in curved components and tubes.

Due to the fact that all dimensional change within CMC components is complete after the pyrolysis step, the manufacture of complex components such as ventilated brake disks and intake flaps is possible through modular construction. Simple building units such as plates, tubes and profiles can be successfully joined within the siliconizing step of the LSI process (in-situ) using a carbonaceous paste with the optional addition of either carbon felt or fabric as the joining material to form complex components. Porous C/C components are prepared and fixed together and molten silicon is caused to flow between the surfaces and react with the carbon material to convert it to SiC and bond the surfaces together. Interlocking the C/C parts prior to siliconizing increases the joining area and leads to a stable assembly which needs no further supports during the reactive bonding in the furnace [6]. In-situ joining is desirable as it eliminates expensive and complicated machining as well as the need for additional metallic bolts or ceramic adhesives.

References

[1] T. Haug, R. Ostertag, W. Schäfer: *Fibre Reinforced Ceramics for Aerospace Applications*, SAMPE European chapter, 1992

[2] W. Krenkel, F. Gern: *Microstructure and Characteristics of CMC Manufactured via the Liquid Phase Route*, ICCM-9, Madrid, Spain, 12-16 July 1993

[3] W. Krenkel, J. Fabig: *Tailoring of Microstructure in C/C-SiC Composites*, ICCM-10, Whistler, Canada, 14-18 August 1995

[4] R. Gadow: *Die Silizierung von Kohlenstoff*, Dissertation, Karlsruhe University, 1986

[5] W. Krenkel, J. Fabig: *Mikrostruktur und Eigenschaften von C/C-SiC Werkstoffen*, Werkstoffwoche '96, Stuttgart, 28 -31 May 1996

[6] W. Krenkel, T. Henke, N. Mason: *In-Situ Joined CMC Components,* CMMC, San Sebastian, Spain, 9-12 September 1996