Fiber-reinforced ceramic matrix composites processed by a hybrid technique based on chemical vapor infiltration, slurry impregnation and spark plasma sintering

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Abstract

Fabrication of multidirectional continuous carbon and silicon carbide fiber reinforced Ceramic Matrix Composites (CMC) by a new short time hybrid process was studied. This process is based, first, on the deposition of fiber interphase and coating by chemical vapor infiltration, next, on the introduction of **silicon nitride** powders into the fibrous preform by slurry impregnation and, finally, on the densification of the composite by **Liquid-Phase Spark Plasma Sintering (LP-SPS)**. The homogeneous introduction of the ceramic charges into the multidirectional fiber preforms was realized by slurry impregnation from highly concentrated and well dispersed aqueous colloid suspensions. The chemical degradation of the carbon fibers during the fabrication was prevented by adapting the sintering pressure cycle. The composites **manufactured** are dense. Microstructural analyses were conducted to explain the mechanical properties achieved. One main important result of this study is that **LP-SPS** can be used in some hybrid processes to densify fiber reinforced CMC.

Keywords: A. Sintering, B. Composites.

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1. Introduction

Non-oxide Ceramic Matrix Composites (CMC), i.e. mainly those consisting of a **silicon carbide (SiC) or silicon nitride (Si_3N_4)** based matrix reinforced with either carbon or SiC-fibers, have the potential for being used up to about 1500°C, as structural materials, in different fields including advanced engines, gas turbines for power/steam co-generation, heat exchangers, as well as nuclear reactors of the future [1,2].

CMC are processed according to (i) gas phase routes (CVI: Chemical Vapor Infiltration) [3], (ii) liquid phase routes either from polymers (PIP: Polymer Impregnation and Pyrolysis) [4-6], or molten elements reacting with mineral charges in the preforms or with the atmosphere (RMI: Reactive Melt Infiltration) [7], or finally (iii) ceramic routes (SI-HP: Slurry Impregnation and Hot Processing) [8-10]. Nevertheless, the time and cost production of CMC are some large obstacles that hamper their wider acceptance. Some hybrid processes, based on the combination of gas, liquid and ceramic routes, have been developed to optimize the densification of the fiber preforms, the microstructure of the composites and to reduce the time and cost production: CVI + (SI-MI or RMI) [11-15], (PIP)_n + CVI [16], CVI + (SI+HP) as the NITE process (for Nano Infiltration of Transient Eutectoid) [17-23]. This last process was oriented to overcome the weakness of composites through other process routes for the improved matrix cracking stress and thermal conductivity [18]. The severe sintering conditions employed in NITE process require quasi-stoichiometric composition SiC fibers of third generation like Hi-Nicalon S, Sylramic or Tyranno SA fibers and thick PyC interphase. $\text{SiC}_f/\text{PyC}_i/\text{SiC}_m$ composites with very low porosity, high mechanical and thermal properties as well as an excellent hermiticity with respect to gaseous cooling fluids such as helium were successfully produced at 1780°C / 20 MPa by NITE process.

In this work, a new short time hybrid process was developed to (i) reduce the time and cost production, (ii) increase fiber preform densification and (iii) optimise the microstructure of the composite. This process is based on CVI fiber coating followed by Slurry Impregnation of ceramic powders into multidirectional continuous fiber preforms and then densification of the composite by Liquid Phase Spark Plasma Sintering (CVI + SI + LP-SPS).

Ex-PAN carbon fiber and SiC (Hi-Nicalon) fiber-reinforced Si_3N_4 matrix composites ($\text{C}_f/\text{Si}_3\text{N}_{4m}$, $\text{SiC}_f/\text{Si}_3\text{N}_{4m}$) were **manufactured**. Carbon fibers were used because of their unique high thermomechanical properties and their low cost, despite the fact that carbon undergoes oxidation at very low temperature (400-500°C). SiC (Hi-Nicalon) fibers of second generation are made of a mixture of SiC-nanocrystals (≈ 5 nm in mean size) and free carbon [C/Si (at) ratio ≈ 1.39] and were chosen for their excellent oxidation resistance and their cost which is about three times cheaper than quasi-stoichiometric SiC fibers of third generation. Hi-Nicalon SiC fibers creep at moderate temperature (1240°C) [24-25] but the soft sintering conditions achieved by SPS may limit their creep. Silicon nitride was chosen as constituent for the matrix because of its excellent thermomechanical properties, such as high strength, hardness, toughness, good shock resistance and good oxidation resistance [26]. First, the CVI technique was used in this process for the deposition of pyrocarbon interphase (PyC) and SiC coating because it yields deposits of relatively uniform composition, structure and thickness even with preforms of complex architecture as those employed in this study. Next, slurry impregnation was used to introduce the ceramic powders into the fiber preforms since this method is cost effective and can be easily employed with fiber preforms of complex shape. Then, **Liquid Phase Spark Plasma Sintering (LP-SPS)** was used to densify the composites since SPS technique allows shorter densification time than traditional techniques which, firstly, is cost beneficial and, secondly,

may limit the chemical reaction of fibers with matrix phases during the fabrication.

Furthermore, to our knowledge, no study has successfully reported the fabrication of continuous fiber reinforced ceramic matrix by Spark Plasma Sintering.

In this paper, the different steps of our hybrid process and the first mechanical characterisations of these materials will be presented and discussed.

2. Experimental method

In order to identify the experimental parameters (pressure, temperature, compounds) of the sintering of composite matrix, first studies are developed on monolithic materials.

2.1. Monolithic matrix process

2.1.1. Ceramic powders

Sub-micronic silicon nitride powders + 7 wt% **yttria (Y_2O_3)** + 3 wt% **alumina (Al_2O_3)** sintering-aid powders were used (**Table 1**). Yttria and alumina sintering-aids react in temperature with the silica layer covering the surface of silicon nitride powders to form a liquid phase that firstly promotes the densification of Si_3N_4 [26], and secondly, may accommodate the stress in the material due to external pressure and, as a result, limit possible fiber damage.

2.1.2. Sintering conditions for the monolithic matrix

Silicon nitride+yttria+alumina powders were mixed by wet ball-milling in polyethylene pots with ethanol and Al_2O_3 balls during 24 hours. Then, mixed powders were dried and milled by dry ball-milling in polyethylene pots during 5 hours to eliminate the agglomerates. The powders were then fitted in a cylindrical carbon die with an inner diameter of 20 mm for Spark Plasma Sintering (Dr Sinter 2080, SPS Syntex Inc.). The

sintering temperature varied from 1500°C to 1700°C, the heating-rate was set to 200°C/min and the holding period varied from 1 to 20 minutes. First, the powders were degassed under vacuum at a temperature of 700°C, next a mechanical pressure of 30 MPa was applied and finally a nitrogen atmosphere ($P_{N_2} = 0.02$ MPa) was introduced in the chamber to avoid Si_3N_4 decomposition at high temperature. The heating process was controlled using an optical pyrometer focused on the surface of the carbon die. It is important to notice that the temperature given is the temperature of the die and this one can be different **from** the temperature of the sample. **Authors claim that the effective temperature is about 50-100°C higher than the one measured on the die surface [27-28].** The linear shrinkage of the **monolithic** matrix during sintering was recorded by an extensometer.

2.2. Composite materials process

2.2.1. Fiber preforms and interphases

The main characteristics of Ex-PAN carbon fibers and SiC Hi-Nicalon fibers are given in **Table 2**. It is well known that fiber/matrix bonding is a key factor controlling performances of ceramic matrix composites, a pyrocarbon interphase (PyC_i) was deposited on the fiber surface from gaseous precursor in order to arrest and deflect the matrix microcracks and to insure a load transfer function [29,30].

To minimize possible chemical reactions of carbon fibers with the matrix constituents during the fabrication, a $SiC_{(c)}$ coating was deposited by CVI on the PyC interphase (PyC_i). The different combinations of PyC interphase, SiC coating and fibers used in this study are: $\{C_f / PyC_i\}$; $\{C_f / PyC_i + SiC_c\}$; $\{SiC_f (Hi-Nicalon) / PyC_i + SiC_c\}$.

2.2.2. Ceramic suspensions and its introduction into the fiber preforms

In order to infiltrate the powder into the preforms, aqueous ceramic suspensions have been realized.

Electrokinetic behaviour of Si_3N_4 powders in aqueous suspension is governed by the ionisation of the surface groups according to the pH and has been extensively studied [31-35]. By acoustophoretic measurement, Jung *et al.* shown that Si_3N_4 M11 Starck powder has a maximum absolute zeta potential value in the pH range [10-11.5] [34]. Hruschka *et al.* studied the evolution of zeta potential versus pH for Al_2O_3 and Y_2O_3 aqueous suspensions and showed that in the pH range [10.5-11.5], Al_2O_3 and Y_2O_3 particles are respectively charged with the same sign as Si_3N_4 particles[35]. As a result, mixed aqueous suspensions of Si_3N_4 + 7 wt.% Y_2O_3 + 3wt.% Al_2O_3 particles were prepared in the pH range [10.5-11.5], being aware that above pH=11 the decomposition of Y_2O_3 particles becomes important [35]. To adjust the pH, tetramethylammonium hydroxide (TEAH, 35 wt% in water, Sigma-Aldrich Chemical Co.) was employed.

The rheological behaviour of the suspensions was investigated with a cone-plate rheometer (Rotovisco RT 20, Haake) by ascending shear rates ramp from 0 to 400 s^{-1} in 5 min to determine the exact pH value for which the viscosity of the suspension is the lowest. To avoid undesired influence from mechanical histories, fresh samples were homogenized by shearing at an identical shear rate of 100 s^{-1} for 1 min and left standing for an additional 1 min prior to measurement.

Different techniques can be used to introduce ceramic particles inside fiber preforms from colloidal suspensions: Electrophoresis Impregnation (EPI) [36], submicronic powder aspiration [37] and slurry impregnation under vacuum. This last method was chosen in this work for its ability to be easily transposed at plant-level to impregnate preforms with

complex shape. The impregnated preforms were then dried during 48h at 25°C. Some samples were cut, polished and characterised by optical microscopy.

2.2.3. Fiber preforms densification by spark plasma sintering

Silicon nitride + sintering-aid powder charged preforms were stacked in a graphite die for SPS. The Spark Plasma Sintering conditions are a compromise between minimizing fibers degradation and achieving full densification. The selection of the sintering conditions was based on the densification of monolithic Si₃N₄. The sintering temperature was 1650°C and hold 2 min at this temperature, while the pressure was varied from 30 to 150 MPa. Fibers degradation can be the result of:

(i) *chemical reactions* of the carbon fibers or pyrocarbon interphase with the matrix phases. Luthra and Park have shown that Al₂O₃ and Y₂O₃ are stable with carbon provided there are no cracks for CO gas to escape [38]. However, silica undergoes carbothermic reduction at 1650°C with p_{CO} < 300 kPa (equation 1). The silicon nitride can react as well with the carbon according to the equation 2.

Silicon carbide can react in a same way with silica or alumina to form CO_(g).

The fast kinetic of densification achieved by Spark Plasma Sintering may limit these reactions. Furthermore the sintering was conducted with the sintering chamber under N₂ atmosphere to limit both possible decomposition of Si₃N₄ and reaction between carbon and silicon nitride (reaction 2).

(ii) *physical degradations* due to the external pressure applied.

Then, to minimize fiber degradation the pressure was applied only when the grain boundary phases began to soften but soon enough (1300°C) to limit gas evolution and thus to inhibit

any possible reaction of Si_3N_4 or secondary grain boundary phases with the pyrocarbon interphase or the fibers [38]. For comparison, some preforms were sintered with the pressure applied at 1500°C instead of 1300°C . Furthermore, to obtain a system as closed as possible to inhibit gas evolution, the preforms were embedded in a powder-bed before loading in the die. To determine the influence of the pressure media on the fiber degradation, a powder-bed of **(boron nitride)** $\text{BN}+\text{Si}_3\text{N}_4$ and a powder-bed of graphite were used.

2.2.4. CMC characterization

The bulk density of the samples was measured by Archimedes method. The microstructures were characterised by scanning electron microscopy (Quanta 400 FEG, FEI) and energy-dispersive X-ray spectroscopy (EDAX) on polished surfaces. Crystalline phases were determined from X-ray diffraction patterns obtained in a θ - θ Bragg-Brentano configuration (D8 advance, Bruker).

The sintered composites were subsequently cut and ground into $45 \times 12 \times 2.5 \text{ mm}^3$ specimens for three-point-bending tests, with a crosshead speed of 0.5 mm/min and a span of 30 mm (Model 5569, Instron Corp). The polished cross sections of the composites before bending tests were characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy on polished surfaces and transmission electron microscopy.

3. Results and discussion

3.1. Monolithic materials

Figure 1 shows the shrinkage and shrinkage rate curves of $\text{Si}_3\text{N}_4 + 7 \text{ wt\% } \text{Y}_2\text{O}_3 + 3 \text{ wt\% } \text{Al}_2\text{O}_3$ during sintering up to 1650°C under 30 MPa . The shrinkage rate curve clearly shows two maximum around 1260°C and 1500°C .

Figures 2 and 3 reveal the phases composition and the microstructures of $\text{Si}_3\text{N}_4 + 7 \text{ wt\% Y}_2\text{O}_3 + 3 \text{ wt\% Al}_2\text{O}_3$ samples sintered at 1260°C with no holding period and at 1700°C after 5 min holding period. Sample sintered at 1260°C is still very porous (65% of theoretical density) whereas sample sintered at 1700°C during 5 min is fully dense (99% of theoretical density) and is constituted of only $\beta\text{-Si}_3\text{N}_4$ grains embedded in an amorphous glassy phase formed from liquid phase solidification. In the 1700°C sintered sample, the glassy phase forms a continuous network which is not the case in the 1260°C sintered sample. The first important increase in density observed around 1260°C can be attributed to particles rearrangement due to liquid phase formation and the second one around 1500°C to a reconstructive α to β phase transition and densification. The isothermal kinetics of densification in the temperature range [1550°C - 1700°C] are reported in figure 4.

A sintering temperature of 1650°C during 1 min allows a relative density of 99 % whereas a sintering temperature below 1650°C does not permit to achieve relative density upper to 68 % even for long sintering period (figure 4). The XRD phase composition of samples sintered 5 min at 1650°C and 1700°C are presented figure 2. Sample sintered at 1650°C is constituted of α and $\beta\text{-Si}_3\text{N}_4$ grains whereas sample sintered at 1700°C is only constituted of β grains. As mechanical properties are changing according to the α/β phase ratio [39], one has to choose the couple of parameters (sintering temperature - sintering time) which corresponds to the required properties. In this study, as fiber-degradation needs to be avoided, a sintering temperature of 1650°C applied during 2 minutes was chosen.

3.2. Composite materials

The minimum in the viscosity of the ceramic powders suspension, **required for infiltration**, occurs for $\text{pH}=10.5\pm 0.1$ (figure 5). As a consequence, the sintering-aids, i.e.

Y_2O_3 and Al_2O_3 powders, were added to the 33 vol.% Si_3N_4 suspensions prepared at pH=10.5. The sintering-aid powders in the Si_3N_4 suspension do not destabilize it (figure 6). After the slurry impregnation step, the inter-tows porosity of the fiber preforms is filled homogenously by the mineral charges (figure 7).

The state of densification **by SPS** of the composites as a function of the applied pressure is presented in the **Table 3**.

When a SiC coating is deposited around the carbon fibers, the pressure required to obtain a full dense matrix is more important than without SiC coating. This lies in the fact that the SiC coating withstands the transmission of the pressure to the matrix. The composite with the SiC coating is fully dense at 150 MPa, but a maximum pressure of 75 MPa is available for large mechanical testing samples due to SPS machine limitations. Hence mechanical tests were carried out on samples sintered at this pressure.

3.2.1. Microstructural characterizations

The microstructures of the composites were studied in term of fiber degradation, densification of the inter and intra-tows matrix, microcracks inside the matrix, decohesion between the fibers and the matrix and will be successively discussed.

SEM micrographs and EDX analyses (figures 8, 9 and 10) reveal the influence of the pressure cycle and of the pressure media on the fiber degradation. When pressure is applied at 1500°C, the carbon fibers embedded in a powder-bed of $\text{BN}+\text{Si}_3\text{N}_4$ are degraded which is not the case when the pressure is applied as soon as 1300°C. Furthermore, when a powder bed of graphite is used instead of a powder bed of $\text{BN}+\text{Si}_3\text{N}_4$ and the pressure applied at 1300°C, the fibers are not degraded. As a result, this confirms that fiber degradation can be avoided by inhibiting gas evolution. This is in agreement with the results obtained by Luthra who observed that Al_2O_3 and Y_2O_3 are chemically compatible with carbon if there is

no cracks for $\text{CO}_{(\text{g})}$ to escape [38]. Furthermore, the chemical composition of the powder-bed have no influence on this degradation. The degradation of the carbon fibers is the result of the chemical reactions between the carbon and the matrix phases, what is confirmed by EDX analysis (figure 9). Indeed, the reaction zone between the fiber and the matrix is constituted of silicon carbide which should mainly be formed according to reaction 2. The SiC (Hi-Nicalon) fibers are chemically degraded after the sintering of the composite (figure 11 and 12). Indeed, the elements Al, Y and O were detected at the periphery of the SiC+C fibers (figure 12). These elements have diffused inside the fiber from the sintering aids liquid phase or from its vapor. No chemical degradation was observed in the carbon fiber composites.

The inter-tows matrix of all composites is fully dense except in some areas located between crossing tows for C-fibers composites (figures 10, 11 and 13). The fiber architecture of the carbon fiber preform which is not the same than the SiC fiber preform is probably at the origin of this partial densification.

In $\text{C}_f/\text{Si}_3\text{N}_4$ composites, the fibers are bonded inside the tows by the pyrocarbon and eventually by the SiC coating whereas in $\text{SiC}_f/\text{Si}_3\text{N}_{4\text{m}}$ composite the thickness of the pyrocarbon interphase and of the SiC coating is too low to bond correctly the fibers. Carbon fiber composites without SiC coating have some intra-tow areas densified by the Si_3N_4 -based matrix. For carbon fiber composites with the SiC coating, the accessibility to the intra-tow porosity is impeded by the SiC layer prior to powder impregnation.

The matrix of the composite is constituted of $\beta\text{-Si}_3\text{N}_4$ grains and $\alpha\text{-Si}_3\text{N}_4$ grains embedded in an amorphous intergranular phase (figure 14).

All $\text{C}_f/\text{Si}_3\text{N}_{4\text{m}}$ composites exhibit microcracks after fabrication but not $\text{SiC}_f/\text{Si}_3\text{N}_{4\text{m}}$ composites (figures 10, 11 and 13). These microcracks are the result of the mismatch

between the **Coefficients of Thermal Expansion (CTE)** of carbon-fibers and Si_3N_4 -matrix. Sabouret *et al.* have computed around 450 MPa the internal stress inside the matrix in unidirectional C fiber-reinforced Si_3N_4 matrix composite (with $E_{\text{C-fiber}}=250$ GPa) [40]. In the multidirectional C-fiber arrangement composites studied here, the repartition of the thermal stress inside the matrix is more complicated than in unidirectional composites but is higher than the intrinsic stress at failure of the Si_3N_4 matrix.

No important decohesion between the fibers and the interphase/coating is observed in carbon fiber composite. In contrast, SiC fiber composites show important heterogeneous decohesions (figure 11). SiC (Hi-Nicalon) fibers are known to creep at moderate temperature (around 1240°C) [25]. Hence, these decohesions can be attributed to strain differences between the SiC fiber and the SiC coating during sintering under pressure at 1650°C . As a consequence, the soft sintering conditions in SPS do not permit to limit enough the fiber strain. In carbon fiber composite the large thickness of PyC interphase can accommodate some strain differences between the constituents of the composite which is not the case in SiC fiber composite due to lower PyC thickness. Furthermore carbon fibers show no important strain. Perspectives to limit the decohesions between the SiC fibers and the SiC coating are (i) to stabilize the fiber microstructure by a heat treatment prior to the SiC deposit [25], (ii) to deposit a thicker PyC interphase between the fiber and the SiC coating, (iii) to formulate a Si_3N_4 based matrix sinterable at lower temperature. These perspectives will be addressed in a further paper.

Some decohesions or cracks between the PyC interphase or the SiC coating and the matrix are observed only in $\text{C}_f/\text{Si}_3\text{N}_{4\text{m}}$ composite. These decohesions are the result of thermal stresses produced by the mismatch between the CTE of the C-fiber and the matrix or by differences between the strain of the fiber preform and the one of the matrix.

3.2.2. Mechanical Behavior

The stress-displacement curves obtained during three-point bending mechanical tests are presented in figure 15. SiC-fibers composites have a brittle behavior with a stress at failure relatively low (≈ 150 MPa). This relatively low stress at failure can be attributed to the chemical degradation of the SiC-fibers during the fabrication, the absence of intra-tows matrix and to some decohesions between interphases and fiber. The brittle behavior is more probably due to the chemical degradation of the SiC-fibers. Other possibilities to explain the brittle behavior are a too thin PyC interphase and/or inhomogeneous bonding areas between the fibers and the SiC coating. C-fibers composites exhibit damageable behavior with the maximum stress at failure around 250 MPa. The presence of the SiC coating around the fibers enhances the mechanical properties. Hypotheses formulated to explain this point are that (i) the strength of the interface bond between the SiC coating and the matrix phases (more precisely the intergranular $\text{SiO}_2\text{-Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ glassy phase) is stronger than the bond between the PyC interphase and the amorphous matrix phase, (ii) as the strain at failure of the composites with and without SiC coating are more or less the same, the increase in ultimate stress for the composite with SiC coating is due to the increase of the elastic modulus of the composite by the SiC coating (iii) the SiC coating prevented the fibers from chemical degradation during the fabrication. However, as fiber degradations were not observed, the last hypothesis is improbable. Characterisations are in progress to better understand the influence of the SiC coating on the mechanical properties of carbon fiber composites. For comparison, a raw preform (i.e. without matrix and not sintered), with a PyC + SiC fiber coating, was mechanically tested (figure 15). Even if the SiC coating contributes to consolidate the fiber preform, the influence of the matrix on the mechanical properties is obvious.

The mechanical behavior of the C_f/Si_3N_{4m} composites **manufactured** by our hybrid process is promising even if their stress at failure around 250 MPa is lower than the 20-years under-development C_f/SiC_m composites fabricated by CVI (≈ 350 MPa) [41]. Experiments should be conducted with different fiber architectures and different thickness of PyC interphases and SiC coating to find the more appropriate ones to this hybrid process.

4. Conclusion

The hybrid process developed here allows short-time fabrication of ceramic matrix composites. Firstly, a mechanical fuse pyrocarbon layer and a SiC coating were deposited around the fiber in the preform by Chemical Vapor Infiltration, secondly, silicon nitride and sintering-aid powders were introduced in the preform by slurry impregnation and, thirdly, ceramic-powder-charged-fiber preforms were consolidated by Spark Plasma Sintering. SiC Hi-Nicalon fiber-reinforced Si_3N_4 matrix composites have a brittle-type mechanical behavior with a relatively low bending stress at failure (≈ 150 MPa) due to fiber chemical degradation and the lack of bond between fibers inside the tows or to some decohesions between interphases and fiber. C_f/Si_3N_4 composites can be produced with no chemical degradation of the fibers if they are embedded in a powder-bed during sintering and if the external sintering pressure is applied soon enough in temperature to inhibit gas evolution and thus fiber degradation. The value of the pressure required to fully sinter the matrix depends on the presence of a SiC coating because this one withstands the application of the pressure inside the preform. The carbon fiber composites show a mechanical damageable behavior and a maximum bending stress at failure around 250 MPa. As a consequence Spark Plasma Sintering can be used in some hybrid processes to densify multidirectional continuous fiber reinforced ceramic matrix composites.

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Figure 1: Applied temperature and pressure, shrinkage and shrinkage rate of the sample during the Spark Plasma Sintering cycle.

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Figure 3:. Si_3N_4 + 7 wt% Y_2O_3 + 3 wt% Al_2O_3 monolithic matrix (a) secondary electron image of sample sintered at 1260°C with no holding period and (b) back-scattered image of fully dense sample sintered at 1700°C during 5 min.

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zone 1 : unreacted matrix zone – zone 2 : reacted matrix and fiber zone.

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Figure 14: TEM images of $\text{C}_f / \text{PyC} + \text{SiC}_i / \text{Si}_3\text{N}_{4m}$ composites showing (a) the different interphases in the materials, (b) $\beta\text{-Si}_3\text{N}_4$ grain, (c) $\alpha\text{-Si}_3\text{N}_4$ grain, (c) the intergranular glassy phase.

Figure 15: Stress/displacement curves from bending test for composites embedded in a powder-bed of graphite and sintered with a 75 MPa mechanical pressure applied at 1300°C.

Table 1: Main characteristics of the fibers used in this study and of Si_3N_4 .

^a At 25°C; ^b Temperature at which $m = 0.5$ in BSR-test; ^c Depending on processing conditions

Table 2: Some characteristics of the powders used.

Table 3: State of densification of the matrix inside the composites as a function of the mechanical pressure applied during Spark Plasma Sintering.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

(b)

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

(a)

(b)

(c)

(d)

Figure 15

Table 1

	Si ₃ N ₄	Y ₂ O ₃	Al ₂ O ₃
provider	HC Starck	HC Starck	Alfa Aesar
grade	M11	C	-
Specific surface area	12-15	10-16	10

(m ² .g ⁻¹)			
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Table 2

	Density	Tensile strength (MPa)	Young's modulus (GPa)	Strain to failure (%)	CTE (10 ⁻⁶ K ⁻¹) ^a	Thermal conduct. (W.m ⁻¹ K ⁻¹) ^a	Creep parameter (T _{0.5})(°C) ^b
Ex-PAN C-fibers	1.77	2100-2400	230-297	1.05-0.71	-0.1 - 10	17	/
SiC Hi-Nicalon fibers	2.74	2800	270	1.0	3.3-3.5	5.0-7.8	≈ 1240
Si ₃ N ₄	3.44	800-1600 ^c	210	≈ 0.004	2.8-3.5	15-40	^c

Table 3

	30 MPa	50 MPa	75 MPa	150 MPa
C _f / [PyC _{i1}] *	partially	partially	full densified	full densified
C _f / [PyC _{i1} +SiC _{c1}] *	partially	partially	partially	full densified
SiC _f / [PyC _{i2} +SiC _{c2}] *	partially	full densified	full densified	full densified
* The thicknesses of PyC _i interphase and SiC _c coating are different in C _f and in SiC _f composites. PyC thicknesses of C _f / [PyC _{i1}] and of C _f / [PyC _{i1} +SiC _{c1}] are the same.				