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Carbon fiber /reaction-bonded carbide matrix for composite materials

- Manufacture and characterization

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ABSTRACT

The processing of self-healing Ceramic Matrix Composites by a short time and low cost process was studied. This process is based on the deposition of fiber dual interphases by chemical vapor infiltration and on the densification of the matrix by reactive melt infiltration of silicon. To prevent fibers (Ex-PAN carbon fibers) from oxidation in service, a self-healing matrix made of reaction bonded silicon carbide and reaction bonded boron carbide was used. Boron carbide is introduced inside the fiber preform from ceramic suspension whereas silicon carbide is formed by the reaction of liquid silicon with a porous carbon xerogel in the preform. The ceramic matrix composites obtained are near net shape, have a bending stress at failure at room temperature around 300 MPa and have shown their ability to self-healing in oxidizing conditions.

Keywords: A. Sintering; B. Composites; C. Mechanical properties; Reaction Bonded Silicon or Boron Carbide (RBSC or RBBC).

1. INTRODUCTION

Non-oxide Ceramic Matrix Composites (CMCs), i.e. mainly those consisting of a SiC or Si₃N₄ based matrix reinforced with either carbon or SiC fibers, have the potential for being used as structural materials at temperatures up to 1500°C, in different fields including advanced engines, gas turbines for power/steam co-generation, heat exchangers, heat treatment and materials growth furnaces, as well as nuclear reactors of the future.¹⁻² CMC are processed according to : (i) the gas phase route (CVI: Chemical Vapor Infiltration),³ (ii) the liquid phase routes either from polymers (PIP: Polymer Impregnation and Pyrolysis),⁴⁻⁵ or molten elements reacting with ceramic charges in the preforms or with the atmosphere

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(RMI: Reactive Melt Infiltration),⁶ (iii) the ceramic route i.e. a technique combining the impregnation of the reinforcement with a slurry and a sintering step at high temperature and high pressure (SI-HP: Slurry Infiltration and Hot Processing)⁷⁻⁸ or finally (iv) some hybrid processes,⁹⁻¹⁶ i.e. a combination of the gas-liquid and ceramic routes in order to associate the advantages of each previous process and to avoid their drawbacks. The conventional ceramic route is a fast densification process, yielding composites with almost no residual porosity and hence a high thermal conductivity. However, the high pressure induces shape and size limitations. The CVI process yields, at low temperature, interphases and matrix of high purity, well controlled composition and microstructure and can be employed in different step of CMC manufacturing (interphases, coatings and matrix infiltration). Furthermore, CVI is a very flexible process: a large number of preforms of different shapes and sizes can be treated simultaneously yielding near-net shape parts. However, it is a costly and a relatively slow technique since it has to be performed at low deposition rate in order to avoid a too rapid sealing of the pore entrance by the deposit and it yields composites with some residual porosity ($\approx 10-15\%$), hence displaying a low thermal conductivity and a poor hermeticity with respect to gas and fluid liquids. The PIP process is, as the CVI, a low temperature process but it is a lengthy technique since several time-consuming PI-P sequences are necessary to achieve an acceptable densification. It yields composites with a significant residual porosity and implies considerable handling. In the MI process or RMI process when the impregnation is reactive (also called Liquid Silicon Infiltration process, LSI) a porous fiber preform is first consolidated with a carbon deposit (either by CVI, PIP or Slurry Infiltration) and next is impregnated with liquid silicon (or a liquid silicon alloy) which climbs by capillary forces in the pore network. Silicon then reacts with the consolidation carbon to yield, in a short time, a composite with a SiC+Si matrix and almost no open residual porosity and hence an excellent hermeticity with respect to gas and liquid fluids as well as a high thermal conductivity. The manufacturing costs of ceramic composites are mainly affected by the processing time, the fiber costs and the machining effort. The hybrid process based on I-CVI and MI is the process that displays, from our viewpoint, the best potential to man-power complex shape CMC pieces in term of time, cost and volume production. Firstly, The I-CVI is the method of choice for the deposition of mechanical fuse and diffusion barrier interphases since it yields deposits of relatively uniform composition, structure and thickness, even in preforms of complex fiber architecture. Secondly, MI is used to fill the residual open porosity of composites prepared by I-CVI to increase both the thermal conductivity and hermeticity. Carbon fibers are used in CMC because of their unique high-temperature mechanical properties and their low cost, despite the fact that carbon fibers undergo active oxidation at

very low temperature ($\approx 350^{\circ}\text{C}$ - 450°C). Carbon fibers based CMC have a microcracked matrix due to the coefficient of thermal expansion mismatch between the carbon fiber (very low and even negative along the axis and positive and relatively high radially) and the ceramic matrix. These microcracks are pathways for the in-depth oxygen diffusion towards the oxidation prone fibers. Solutions developed to utilize CMC in oxidizing atmosphere are the utilization of the far more expensive SiC fibers¹⁷ or, for C-fiber reinforced ceramic matrix the utilization of Environmental Barrier Coating (EBC),¹⁸⁻²⁰ and/or self-healing interphases and matrix.²¹⁻²² The concept of self-healing materials is based on the introduction of elements inside the materials forming fluid oxide phases in a wide range of temperature that can fill the cracks, rendering the whole materials self-healing. Self-healing mechanisms are mainly achieved by introduction of boron species efficient at relatively low temperature ($500\text{-}1000^{\circ}\text{C}$) and silica-rich phases efficient at high temperature ($1000\text{-}1500^{\circ}\text{C}$) (equations 1 to 4).²²

Self-healing interphases and self-healing matrices have been successfully deposited inside fiber preforms by I-CVI process.²¹⁻²² The need for low cost CMC required the development of short time and cost-effective processes. In this paper a hybrid process was studied to develop a fully dense matrix which is able to slow down oxygen diffusion towards the oxidation prone carbon fibers by healing the cracks. This process consists in (i) depositing a pyrocarbon mechanical fuse and a SiC diffusion barrier on carbon-fibers by CVI, (ii) introducing boron carbide and alumina powders into the fiber-preform by slurry infiltration, (iii) forming a porous carbon xerogel network between the powder particles by a sol-gel process and, next, (iv) consolidating the fiber-preform by reactive melt infiltration of silicon which bonds alumina and boron carbide particles and react with the porous carbon to form silicon carbide (equation 5).

The self-healing matrix fabricated is then made of reaction bonded boron carbide (RBBC), reaction bonded silicon carbide (RBSC), residual free silicon and alumina phases.

In this study, aluminium element is introduced in the matrix to reduce the volatilisation of boron species at high temperature in the presence of water vapor.²³ The processing and properties of reaction bonded silicon carbide, reaction bonded boron carbide and composites processed by liquid silicon infiltration have been reported by several authors.²⁴⁻³⁶ One of the main challenges in processing reaction-bonded silicon carbide is that the porosity of carbon to be infiltrated must be low enough to minimize free silicon content, but high enough to avoid the shocking-off phenomena i.e. the stop of silicon impregnation due to

the full filling of the porosity by the formed silicon carbide phase. The minimum amount of porosity required to avoid shocking off phenomena depends of the density of the carbon and can be calculated by the formula [1],³⁷ where V_i , M_i and d_i are respectively the volume fraction, the molar weight and the density of the species i .

$$V_{SiC} = \frac{M_{SiC} \cdot V_c \cdot d_c}{M_c \cdot d_{SiC}} \quad [1]$$

In the case of carbon xerogel the density was measured and its value is around 1.65. By assuming that the volume fraction of SiC is maximum ($V_{SiC} = 1$), V_c calculated equal 58% and, as a result the porosity has to be higher than 42% to avoid shocking-off phenomena. The carbon phase is usually obtained by the pyrolysis of phenolic resin or pitch. The pyrolysis of pitch leads to the covering of the pore surfaces whereas the pyrolysis of resin usually leads to pieces of cokes which cannot be totally transformed into SiC by reaction with silicon. Porous carbon can be obtained from furfurylique resin and foaming agent as patented by Hucke.³⁸ In this work, porous carbon is formed by a sol-gel process from resorcinol and formaldehyde to form a RF xerogel.³⁹ This method was chosen for its ability to easily tailor the porosity of the carbon xerogel by adjusting the synthesis parameters (amount of reactants, nature and amount of catalyst, gelification, drying and pyrolysis parameters). The microstructure is based on a continuous silicon carbide networks to allow good strength at high temperature and to limit matrix creep. The aims of this paper are, firstly, to present and discuss the different steps of the hybrid process developed as well as some chemical, physical and mechanical properties of the fabricated CMC and, secondly to compare the mechanical properties of the CMC processed by our short time, scalable, cost-effective hybrid process developed with the ones processed by the costly but high effective CVI process.

2. EXPERIMENTAL PROCESS

2.1 Fiber preforms and dual interphases of PyC/SiC

The main characteristics of Ex-PAN carbon fibers are given in Table 1. It is well known that fiber/matrix bonding is a key factor controlling performances of ceramic matrix composites⁴⁰⁻⁴². In order to arrest and deflect the microcracks of the matrix and to insure a load transfer function, a pyrocarbon interphase (PyC_i) was deposited by CVI on the fiber surface from propane (according to equation 7a).

To minimize possible chemical reactions of carbon fibers with silicon melt during the fabrication, a SiC coating was deposited on the PyC interphases by CVI according to equation 7b.

2.2 Slurry preparation

Commercial boron carbide (grade F15, HC Starck) and alumina (Alfa Aesar) powders were used and their size distributions are reported in Figure 1. Mixed boron carbide+alumina aqueous suspensions were prepared using electrosteric dispersion mechanism by the addition of polyethylenimine dispersant (PEI, Sigma-Aldrich). Suspension compositions are given in Table 2.

2.3 Introduction of the ceramic particles into the fiber preforms

Different techniques can be used to introduce ceramic particles inside fiber preforms from colloidal suspensions: Electrophoresis Impregnation (EPI),⁴³ submicronic powder aspiration⁴⁴ and slurry infusion 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.

2.4 Formation of porous carbon inside the preform

Xerogels with different synthesis parameters were studied to find the most appropriate one for the impregnation by liquid silicon and the conversion in silicon carbide. The molar resorcinol / formaldehyde ratio (R/F) was fixed to 1/2, the solid content (R%) was varied from 20 to 40 % and the catalyst (sodium carbonate) content was given by the molar resorcinol / catalyst ratio (R/C) and varied in the range [2000, 5000]. Resorcinol was added to formaldehyde and the mixture was stirred for 15 min. Sodium carbonate was dissolved in deionised water to form a separate solution. The two solutions were then mixed and stirred during 24 hours, introduced in the fiber preform and left 1 hours under vacuum, then a gelification period in a closed system at 65°C during 48 hours happened followed by a drying period at 85°C during 48 hours and a pyrolysis step in argon atmosphere at 950°C.

2.5 Fiber-preforms densification by Silicon Melt Infiltration (MI)

The experimental arrangement used to realize infiltration of silicon inside the fiber preform is schematically shown in Figure 2. The utilization of a carbon-weaving between the fiber-preform and silicon aims to avoid machining of the composite after the elaboration. The zirconium lump is used to obtain a low partial pressure of oxygen during the thermal treatment (at equilibrium between Zr and ZrO₂, $p_{O_2} = 10^{-24}$ atm) in order to avoid oxidation of the surface of the melt and to promote wetting. The melt infiltration was realized under vacuum during 30 min at a temperature slightly above the melting point of silicon. Indeed, to avoid to trap some gaseous species inside the material, it is necessary that the flow of silicon raising by capillarity inside the material be low enough.⁴⁵ A low flow can be achieved by a low

σ/η ratio where σ and η are respectively the interfacial tension and the viscosity of the melt (Figure 3).⁴⁶ Thus, the melt infiltration was conducted at 1420°C.

2.6 Characterization

The microstructures were characterized by scanning electron microscopy and energy-dispersive X-ray spectroscopy on polished and HF-HNO₃ chemical-etched surfaces (Quanta 400 FEG, FEI; EDAX). Porosity was determined by Hg-porosimetry (Micromeritics, AutoPore IV). Crystalline phases were determined from powders by X-ray diffraction patterns obtained in a θ - θ Bragg-Brentano configuration (D8 advance, Bruker). Mechanical properties at room temperature were determined by bending tests and tensile tests. Three point bending tests were performed on 45x12x2.5 mm³ parallelepiped samples with a crosshead speed of 0.5 mm/min and a span of 30 mm (Model 5569, Instron Corp). Tensile tests were based on unloading-reloading cycles at several levels of strain in order to follow (i) changes in the damage with change in the longitudinal elastic modulus and (ii) the intensity of the work of friction occurring at the interfaces which is related to the hysteresis loops.

3. RESULTS AND DISCUSSION

3.1 Introduction of the ceramic powders and formation of the porous carbon network into the fiber preforms

After the under-vacuum slurry infusion step, the inter-tows porosity of the preform is filled homogeneously by the mineral charges, as can be seen from Figure 4. Xerogel with different porosity were prepared and impregnated by melted silicon (Figure 5). It clearly appears from Figure 5 that the dimension, the interconnectivity and the content of free silicon can be tailored by properly choosing the porosity of the initial carbon xerogel. When the porosity of the xerogel is below 42%, shocking off phenomena occur. The value calculated is in agreement with this fact. Figure 6 shows that the pore size of the porous carbon can also be tailored by adjusting the processing parameters of the xerogel. A microstructure of a carbon xerogel is seen in Figure 7 where the carbon and the porosity networks clearly appear.

3.2 Fiber-preforms densification by Silicon Melt Infiltration (MI)

Complete infiltration of silicon inside the fiber preform occurs only if a preliminary thermal treatment just below the melt temperature of silicon takes place. During this thermal treatment, species are desorbed from the powders and the silicon carbide coating is desoxydized (equations 8 to 10). Furthermore, silicon vapor can condensate on the preform surface which will promote its further wetting by the molten silicon.

The formation of carbon xerogel inside the preform leads to a continuous network of silicon carbide according to equation (5), which is not the case without introduction of carbon inside the preform prior to silicon impregnation (Figure 8). The formation of silicon carbide decreases the free silicon content in the materials and hence enhances the mechanical behavior in temperature. Silicon carbide in the composite prepared without carbon xerogel is formed by a dissolution-precipitation mechanism.³⁵ The porosity distribution of the fiber preform at the different state of its process is presented in Figure 9 and the microstructure of the composites in Figure 10. The pore size inside the tow of the fiber preform is between 0.1 to 10 μm whereas the inter-tows porosity size is between 10 to 300 μm . The boron carbide and alumina powders are present inside the inter-tows matrix but not in the intra-tow matrix. This is due to a too low pore size entrance for the powders. After the powder introduction, the pore size of the preform is mainly around 0.08 μm and is filled by carbon xerogel after its introduction and its pyrolysis. The dense matrix is made of boron carbide, silicon carbide, free silicon, alumina and it fills homogeneously the inter-tows porosity of the fiber-preform. The intra-tow porosity is filled by silicon. No fiber degradation was observed, nor decohesion between the fibers and the matrix. The matrix is in a microcracked state after elaboration due to the coefficient of thermal expansion mismatch between the carbon fibers and the matrix phases. The sealing of these cracks by the self-healing phases in oxidizing conditions was studied.

3.3 Self-healing behavior

Figure 10b reveals the morphology of a polished section of the composite exposed 13h at 700°C in air. The healing of the matrix cracks can be clearly observed (encircled on Figure 11). At 700°C the sealing of the cracks is due to the formation of B_2O_3 liquid phase and is favorable to impede the in-depth oxygen diffusion towards the oxidation prone fibers. For oxidation treatment at 600°C during 15 hours the cracks are not fully sealed due to incomplete formation of B_2O_3 (Figure 10a). Indeed, at 600°C, its formation rate remains slow and respectively its volatilization rate significantly high due the reaction of B_2O_3 with moisture in air ($P_{\text{H}_2\text{O}} \approx 1 \text{ kPa}$).⁴⁸ For temperature of 1100°C, the cracks are sealed by an amorphous protective and stable Si-B-O-Al phase. Indeed this sealing phase is chemically stable in a purely corrosive environment ($\text{H}_2\text{O}/\text{Ar}$) at 600°C (Figure 12).

3.4 Mechanical behavior

The mechanical behavior of the composites studied at room temperature is given in Figure 13. The composites elaborated show a high bending stress at failure (≈ 300 MPa). At room temperature, there is no significant difference observed between the composite processed with or without carbon xerogel. This can be explained by the facts that the fibers are mainly responsible of the ultimate stress of the composite. As a result, the tensile mechanical properties at room temperature which will come after were determined on composites processed without formation of carbon-xerogel. The mechanical behavior in temperature of the composite processed with and without carbon xerogel formation will be given in a further paper. From the tensile curves (Figure 14), at the beginning of the tensile loading, no linear elastic behavior is observed which is due to the microcracked state of the composite after processing (Figure 10). Damage initiation in ceramic-matrix composites is often a critical step in their mechanical behavior. The crack propagation has to be controlled in order to avoid catastrophic rupture. The fact that the composite is already damaged at the end of the processing stage may be considered as a sign that the material is able to withstand further damage. Such a composite exhibits a higher mechanical reliability than undamaged materials. The loading-unloading cycles indicate an intensification of the hysteresis loops with strain accumulation which is related to an increase of the friction area. The small drop in composite stiffness characterized by the tangent modulus, attests the progressive feature of the damage. The residual strain accumulation after unloading is related to the thermal stress relaxation coming from the processing stage. The composite surface rupture shows multiple crack deviations at the interfaces with the extraction (pull-out) of the fibers (Figure 15). Such morphology of fracture surface implies a high energy dissipated by friction at the interfaces.

The stress at failure of our composites have to be compared with the stress at failure of our reference composites which are a C_f/SiC composite and a $C_f/Si-B-C$ composite with a multilayered self-healing Si-B-C matrix processed by Chemical Vapor Infiltration. It clearly appears on the figure 15 that the mechanical behaviour at room temperature of the composite fabricated by the hybrid process is similar to the one of our reference composites processed by CVI. The next step of our works will be, first, to determine how the formation of a silicon carbide network by the reaction between silicon and carbon xerogel positively influence the mechanical properties in temperatures and, second, to determine the lifetime of the composites processed by our hybrid process under oxidizing conditions and to compare it with the lifetime of carbon fiber reinforced self-healing Si-B-C ceramic matrix processed by CVI.²² This will be addressed in a further paper.

4. CONCLUSION

Ceramic matrix composites with a self-healing matrix were successfully processed by a low cost, short-time, near-net-shape and scalable process based on the reactive melt infiltration of silicon into a fiber preform containing boron carbide+alumina powders and a porous carbon xerogel. The microstructure of the matrix was optimised by properly choosing the porosity of the carbon xerogel to minimize the content of free silicon, to optimize its distribution and to avoid the phenomena named shocking-off. The shocking-off phenomena corresponds to the fact that the infiltration by silicon in the liquid state is stopped, due to the increase in volume of the formed silicon carbide which occupies too much space and fills up the porosity. The good impregnation of liquid silicon into the preform was possible only if this one was heat-treated at a temperature just below the melting point of silicon. This was attributed to the desorption of gaseous species from the powders and to the desoxidation of silicon carbide coating. The self-healing matrix fabricated is made of reaction-bonded silicon carbide, reaction-bonded boron carbide, and residual free silicon. The ceramic matrix composite processed has a high bending stress at failure (≈ 300 MPa) and has shown its ability to self-healing in oxidizing conditions.

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Figure 1: Particle size distribution of the powders

Figure 2: Experimental arrangement used to realize the infiltration of silicon inside the fiber-preforms. (1) fiber-preform; (2) carbon weaving; (3) silicon lumps; (4) zirconium lump; (5) BN-covered carbon crucible

Figure 3: Evolution of σ/η ratio vs temperature for silicon melt (according to Kimura *et al.*⁴⁷)

Figure 4: Micrographs of fiber preforms (a) before impregnation by the ceramic powders and (b) after impregnation. $B_4C+Al_2O_3$ powders correspond to light grey contrast between the tows in (b).

Figure 5: Optical microstructure of reaction bonded silicon carbide fabricated from carbon xerogels whose porosity before silicon impregnation is (a) 78%, (b) 62%, and (c) 36%. Silicon corresponds to the light grey contrast and silicon carbide to the dark grey contrast.

Figure 6: Pore size distribution of different porous carbon xerogels.

Figure 7: SEM microstructure of a porous carbon xerogel.

Figure 8: Microstructure of the matrix of the composite after liquid silicon infiltration (a) without addition of carbon xerogel, (b) with carbon xerogel. Samples etched in HF/HNO₃ solution to remove free silicon. Boron carbide corresponds to the dark grey contrast, silicon carbide to the white in (a) and light grey contrast in (b).

Figure 9: Porosity distribution in the fiber preform at the different states of its process: (a) before the introduction of the powders, (b) after the introduction of the powders, (c) after the formation of carbon xerogel, and, (d) after impregnation by silicon melt.

Figure 10: SEM micrographs of $C_f/B_4C-SiC-Si-Al_2O_3$ composite processed with carbon xerogel, (a) low, (b) medium, (c) large magnification. Boron carbide corresponds to the dark grey contrast, silicon carbide to the light grey contrast and silicon to the white contrast.

Figure 11: SEM back-scattered micrographs of $C_f/B_4C-SiC-Si-Al_2O_3$ composite processed with carbon xerogel after oxidation under air at (a) $600^\circ C-15h$, (b) $700^\circ C-13h$, and (c) $1100^\circ C-30min$.

Figure 12: SEM back-scattered micrograph of $C_f/B_4C-SiC-Al_2O_3-Si$ composite processed with carbon xerogel after oxidation under air at $1100^\circ C-30min$ and a thermal treatment at $600^\circ C$ during 70 hours under H_2O/Ar ($P_{H_2O}=10\text{ kPa}$) to study the stability of the oxide self-healing phase under wet atmosphere.

Figure 13: Bending stress at RT of the $C_f/B_4C-SiC-Si-Al_2O_3$ composites processed with and without carbon xerogel.

Figure 14: Tensile stress at RT of the $C_f/B_4C-SiC-Si-Al_2O_3$ composites fabricated by the hybrid process without carbon xerogel and of our reference composites processed by CVI.

Figure 15: SEM image of the surface rupture of the CMC showing the fiber debonding from the matrix

Table 1: Main characteristics of the carbon-fibers used in this study.

Table 2: Description of the composition of the suspension.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 12

Figure 13

Figure 14

Figure 15

Table 1

Density	Tensile strength (MPa)	Young modulus (GPa)	Strain to failure (%)	CTE (10^{-6} K^{-1})	Thermal conduct. ($\text{W.m}^{-1}\text{K}^{-1}$)
1.77	2100-2400	230-297	1.05-0.71	-0.1 // $10 \perp$	17

Table 2

Composition of the suspension
28 vol.% B_4C + Al_2O_3 suspension
Solvent = deionized water
(Al_2O_3 / B_4C) weight ratio = 0.2
PEI = 1.5 wt.% of dry powders