IMPROVED SiC / SiC AND C/C MATERIALS APPLICATIONS PARTS.
EUROMAT 2005

Authors: I. Berdoyes, J. Thebault, E. Bouillon
Snecma Propulsion Solide (SAFRAN Group)
Les cinq Chemins – 33187 Le Haillan – France

Abstract:

For a long time, silicon carbide composites are very attractive materials for fusion applications. Since 1990's Snecma Propulsion Solide is involved in such specific materials trying to adapt constantly the materials to such demanding working conditions.

Starting from an industrial basis of producing ceramic matrix composites for aeronautics, we have improved mechanical and thermal properties of SiC/SiC composites by modifying its textile reinforcement. With these textures, we have produced and tested generic parts (U,T C,O shape types).

We have also tested different joining technologies; these results will be presented.

In parallel, Snecma Propulsion Solide has developed Carbon/Carbon composites materials for the divertor. The composites materials evolutions are also described.

1. INTRODUCTION

Producing energy from nuclear reactors requires, behind the plasma facing components, a breeding blanket, which associates tritium generation, cooling and vapor generation for turbines. These three functions need specific parts made of high performances materials. In fact, these materials have to withstand high temperatures (<1300°C), high mechanicals loads, high thermal gradients, and high neutrons fluxes…. Ceramic materials are well suited for these applications, and especially silicon carbide (SiC) mainly for its thermal properties and its irradiation behavior (low atomic number, low activation, limited neutron flux sensitivity).
Ceramic materials are brittle. To overcome this major drawback, Snecma Propulsion Solide, SAFRAN Group, (originally SEP) has developed, since the 80's, Ceramic Matrix Composites materials with a non-brittle behavior and resisting to high temperature. Those composite materials are named "thermostructural materials".
Then, thermostructural Ceramic Matrix Composites made of SiC fibers linked together with SiC matrix (SiC/SiC) are prime candidates for breeding blanket for fusion reactors.

At the same time, Snecma Propulsion Solide has developed specific enhanced carbon / carbon composite materials for plasma facing components, Divertor for example, based on the experience from rocket nozzle manufacturing.

2. IMPROVEMENT OF THERMO-STRUCTURAL CERAMIC MATRIX COMPOSITES (CMC) MATERIAL FOR BREEDING BLANKET APPLICATION.

At the beginning, the SiC/SiC composite materials were manufactured from a bi-dimensional (2D) reinforcement using standard grade SiC fibers.
These materials have been defined in order to obtain good mechanical characteristics in the fiber plane. Due to their 2D structure those materials suffer from insufficient properties in the third direction, which generate sensitivity to delamination, low thermal conductivity and mechanical properties in thickness. These drawbacks lead to difficulties in components assembly and tightness.
We will present here the improvements we get on fiber reinforcement, sub element assembly and manufacturing, and tight CMC heat exchangers.

2.1. Optimized fifer reinforcement

Our 2D experience highlighted the necessary development of a new fiber preform based on multi layer reinforcement technology, to avoid delamination risks. These multi layer woven fabrics, are branded GUIPEX® by Snecma Propulsion Solide. The number of layers, linked together, is adjustable, in order to obtain a composite thickness range between 2 to 7 mm, or variable thickness. Furthermore, these reinforcements can be optimized to obtain orthotropics composite materials, with in-plane characteristics close to a 2D material. As reported in table 1, the resulting Nicalon fibers composites exhibit characteristics in-plane similar to previous 2D SiC/SiC [1]. This reinforcement has been applied to manufacturing complex shape as shown in figure 1. Then the Guipex® structure for CMC brings high properties in a third direction conserving the good properties of 2D SiC/SiC materials.

Table 1. *Comparison between 2D and Guipex® Nicalon composite.*

Characteristics		*Nicalon 2D SiC/SiC N2-1*	*Nicalon Guipex® SiC/SiC N3-1*
Density	[g/m^3]	> 2.4	2.5
Porosity	[%]	10	12
σ_{11}	[MPa]	285	300
ε_{11}	[%]	0.75	0.60
E_1	[GPa]	200	220
λ_3	[W/m.k]	9	9

Fig. 1. *Example of complex CMC component (flame holders for military engine).*

In terms of tensile strain through the thickness and interlaminar shear stress, the benefit of GUIPEX® is demonstrated by a subsequent decrease in the values scattering compared to 2D composite materials. And, it has been also underscored that a significant increase of these mechanical characteristics are very beneficial to better optimize the design of complex shapes.

More recently, considering the know-how achieved with GUIPEX® reinforcements and the large possibility provided by current fabrics hardware, Snecma Propulsion Solide engaged a development of new GUIPEX® multilayer woven fabrics, to increase the mechanical potential of the resulting composite materials and also thermal conductivity in the thickness direction (“3”).

A large variability of reinforcement was explored. Some of these are summarized in table 2 [2].

Table 2. *New multilayer preforms informations (detailed description is proprietary).*

Ref	*Brief description*
A (N3-1)	multilayer weave base
B	modified links
D	increasing of linked rate
N	Interlock type
H	"evolutive" reinforcement
M	3D ortho type

With these fabrics, SiC/SiC materials were performed, using standard Snecma Propulsion Solide densification process. : Chemical Vapor Infiltration (CVI) This process is well adapted to densify textures.

Thermal conductivity, at room temperature has been calculated taking into account the measured thermal diffusivity and the measured thermal heat capacity (table 3). In direction 1 (in plane), there is no major variation between the composite materials. In the third direction, the effect of the reinforcement is more outlined. These variations are, in first approximation, the resulting effect of the fiber arrangement in the composite material. For example, the 3D ortho preform, which is characterized by the highest fiber volume ratio, in direction 3 (through thickness), showed the highest conductivity in this direction.

Table 3. *Nicalon CMCs thermal conductivity at room temperature*

SiC/SiC material	l *in dir 1 [W/mk]*	l *in dir 3 [W/mk]*
SiC/SiC A	25	9
SiC/SiC B	23	16
SiC/SiC D	27	15
SiC/SiC N	25	14
SiC/SiC H	25	10
SiC/SiC M	-	18
SiC/SiC 2D		9

For all composites, the in plane tensile stress level is high and comparable to 2D material (table 4). The highest value is obtained with the interlocked type composite.

Table 4. *Tensile stress, in direction 1 at room temperature for SiC/SiC composites*

SiC/SiC material	s_{11} *[MPa]*	e_{11} *[%]*	E_1 *[GPa]*
SiC/SiC A	300	0.60	220
SiC/SiC B	275	0.55	200
SiC/SiC D	280	0.60	220
SiC/SiC N	340	0.75	240
SiC/SiC H	310	0.60	230
SiC/SiC M	250	0.45	180
SiC/SiC 2D	285	0.75	200

Tensile strength properties in direction 3 and interlaminar shear (ILS) stress were also measured at room temperature. Data are reported in table 5. The most interesting effect of the reinforcement type can be observed on these two characteristics. In fact, compared to the reference value of the SiC/SiC high levels of σ_{33} and ILS have been obtained with B, N and M GUIPEX® composite material type. These promising results open interesting opportunities in designing parts submitted to complex loads.

Table 5. *Tensile stress in direction 3 and interlaminar shear, at room temperature, for SiC/SiC composite*

SiC/SiC material	s_{33} *[MPa]*	*ILS [MPa]*
SiC/SiC A	5	25
SiC/SiC B	12	58
SiC/SiC D	12	33
SiC/SiC N	16	52
SiC/SiC H	8	37
SiC/SiC M	31	81

2.2. Sub element assembly manufacturing

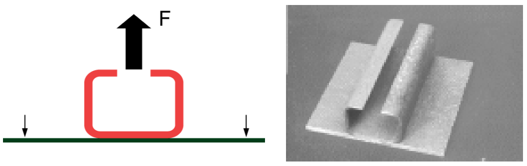
Sub elements developments manufacturing is required to demonstrate the capability to achieve geometric singularities like curvature radius, stiffeners, holes, and thickness variations of the fiber architecture, thus giving responses to functional design requirements or needs [3, 4]. Continuum Damage Mechanics models have been developed and validated for bulk stresses and strains analysis. Sub element testing offers a technological answer to design criteria and stresses allowable.

Thus, 6 kinds of sub elements were manufactured for feasibility check out (small radius, thickness variation, stiffeners, "C", "T" shapes) and were submitted to various mechanical testing for finite elements analysis model validation.

Sub element # 1 is representative of a stiffened plate (Fig. 2), manufactured with a specific GUIPEX® reinforcement. A rather good correlation is obtained between the calculated rupture and the experimental rupture.

Fig. 2. Subelement #1 test

Subelement # 1

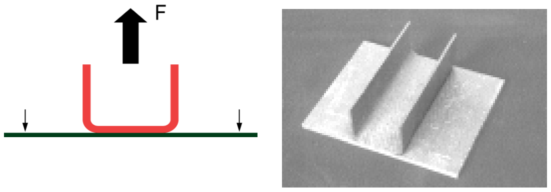


Calculated rupture:	Experimental rupture:
F = 50 daN	F = 56 daN

Figure 3 shows the sub element #2. It is similar to sub element # 1, including an additional reinforcement between the plate and the stiffeners by fiber stitching. A significant increase of rupture can been observed by the stitching operation.

Fig. 3. Sub element #2 test

Sub element # 2

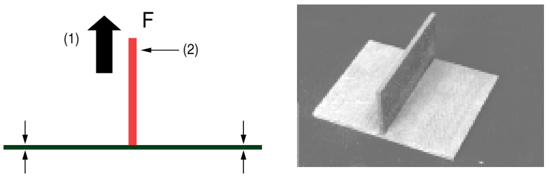


Calculated rupture:	Experimental rupture:
F = 50 daN	F = 110 daN

Sub element # 3 is a T shape (Fig. 4), manufactured with GUIPEX® preforms and SiC fiber stitching. The correlation between calculation and experimental test is not satisfying. In this case, the stitching reinforcement is not taken into account by the model.

Fig. 4. Subelement #3 test

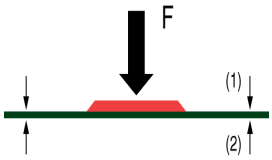
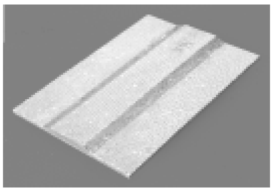
Subelement # 3



Calculated rupture:	Experimental rupture:
(1) F = 30 daN	(1) F = 110 daN
(2) F = 25 daN	(2) F = 42 daN

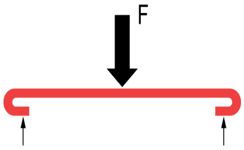
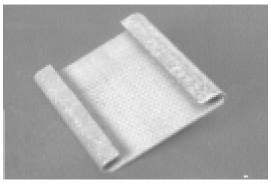
Sub element # 4 (Fig.5) is an one-piece plate with a thicker local area, directly obtained by GUIPEX® weaving.

Fig. 5. Sub element #4 tests

Sub element # 4	
	
	Experimental rupture: (1) F = 90 daN (2) F = 160 daN

Sub element # 5 is a C shape panel (Fig.6).

Fig.6. Sub element #5 test

Sub element # 5	
	
Calculated rupture: F = 70 daN	Experimental rupture: F = 112 daN

In conclusion GUIPEX® textures are able to be used in complex forms and assembly, opening the way to manufacture very complex shapes required for example for a breeding cooling system.

From Snecma Propulsion Solide long-term experience with composites, it appears clearly that it is absolutely necessary to go to manufacture and test representative sub elements to get the real potential of parts and local singularities.
This is also the only way to be confident in thermomechanical results of the complex modelisation and analysis. This is Snecma Propulsion Solide working methodologies, considering that a composite material exits only through a representative part.

2.3. Tight CMC heat exchangers

CMC materials have a lot of interesting thermal and mechanical properties. Due to the particular processes used for their manufacturing (cf. polymer impregnation and pyrolysis, chemical vapor infiltration…), they are always porous. This porosity, in the range of 10%, is an open porosity and that means that if these materials are used to make parts as heat exchangers, there will be an unacceptable leak rate through the wall.

Snecma Propulsion Solide developed different technologies to coat these materials with an impervious SiC coating. Helium leak rate can be lowered to $1x10^{-6}$ $Pa.m^3/s$ and also be as tight as metal ($< 10^{-9}$) in some configurations.

Heat exchangers are generally manufactured by assembling different parts and sub elements.
So, Snecma Propulsion Solide studied the brazing of CMC materials on themselves and on metals.

In the field of aerospace applications for C/SiC composites, Snecma Propulsion Solide manufactures heat exchangers one with metallic tubing (Fig. 7) for cryogenic temperature and the other one is a whole CMC panel for high temperature (Fig.8, 9).

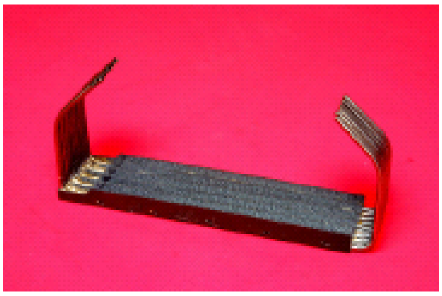


Fig. 7: brazed CELL-22 specimen [5]

Fig. 8: AC3 concept [5]

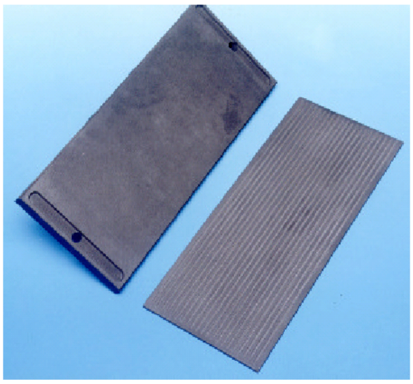


Fig. 9: AC3 panel ($380x157\ mm^2$) [5]

Three channels whole ceramic heat exchanger has been successfully tested up to 1.2 $MegaWatt.m^{-2}$ (with JP7 cooling) [5].

3. IMPROVEMENT OF THERMO-STRUCTURAL MATERIAL FOR PLASMA FACING COMPONENTS.

Since the beginning of the 90's, Snecma Propulsion Solide is involved in nuclear fusion applications through its high performances C/C composite materials.

The major components of a fusion reactor include in particular first wall, divertor and blanket.

The Plasma Facing Components are exposed to high fluxes of energetic plasma particles and it can receive a large fraction of plasma energy in the event of a disruption.

While corroding the divertor, the plasma is polluted. So, to limit the pollution, chemical elements with high atomic number are excluded. Also, current reactors are mainly equipped with graphite and carbon-carbon composites materials.

The thermal flows are very high and conductive materials are required.

The carbon-carbon composite material is one of the possible candidates. The main reasons for the choice of carbon as PFC are:

- Low atomic number (pollution of the plasma),
- Refractory,
- Thermal shock resistance,
- Good thermal conductivity,
- Compatibility with the plasma.

3.1 Composite materials developed by Snecma Propulsion Solide

Thanks to his 40 years experience in manufacturing C/C parts for rocket propulsion, Snecma Propulsion Solide, originally SEP developed specific materials and assemblies for fusion applications [6, 7].

Starting from the specific requirements, we develop and select the best composite materials.

Different parameters can be adjusted, for example, the reinforcement: nature, orientation, fibers ratio. The matrix can also be adjusted: nature, volume ratio.

For fusion applications we developed different materials:

- N11: first material used for fusion
- N112: Evolution of N11- higher density
- N21: Higher conductivity material
- N31: Higher conductivity material
- NB31: N31 completed with carbon impregnation
- NS11: N11 doped with Si
- NS31: N31 doped with Si.
- NB41: Higher conductivity material

The C/C composite materials are branded Sepcarb®.

Sepcarb® reinforcement:

N11 is a 3D CFC, made with an ex-PAN Novoltex® preform. The fraction per volume of fibers is about 30%. The densification is made by chemical infiltration of pyrocarbone followed by a heat treatment at high temperature.

N11 and N112 were the first generation of materials. To improve thermal properties, new materials were developed. There are N21 and N31. For those materials, higher conductivity fibers are used.

In order to reach the specified thermal conductivity, unbalanced textures were developed with high characteristics carbon fibers and very conductive pitch based carbon fibers. The particularities of the two materials are the nature and the organization of the fibers. These materials are N21 and N31. The fraction of fibers is about 35% per volume. The texture is unbalanced to favor the conductivity in one direction.

Actually, Snecma Propulsion Solide has developed a new material with a new fiber with better characteristics.

This new material is called NB41.

Sepcarb® densification:

One of the key properties of the material for nuclear fusion is the thermal conductivity. Densification obtained by CVI of pyrocarbon followed by high temperature treatment gives to the Sepcarb® high thermal and mechanical characteristics.

The use of pure carbon as PFC brings up two majors problems: the erosion and the retention of tritium.

To reduce these problems, three options have been identified:

1) Increase of the density. In this case, the CVI densification is completed with carbon impregnation.

2) Increase the conductivity.

3) Dope the material with silicon.

The last solution is very interesting because of:

- Very good resistance to oxidation,
- Diminution of radiation enhanced sublimation,
- Decrease of tritium retention,
- Improvement of resistance to oxidation in relation to H_2O and O_2 impurities.

Improvements of the process have been also developed to reduce the manufacturing cycle.

Snecma Propulsion Solide materials

The following charts show the main Snecma Propulsion Solide Composites materials used for nuclear applications (Fig.10).

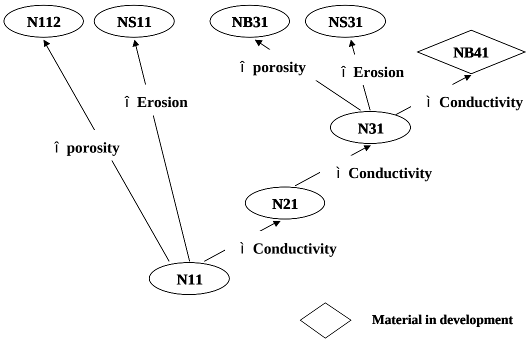


Fig. 10: Evolution of the Snecma Propulsion Solide composite materials

Today, N11 Sepcarb® fits out the Tokamak Tore Supra in the first wall. NB31 is good candidate for the W7-X and for Tokamak ITER Divertor Target Elements.

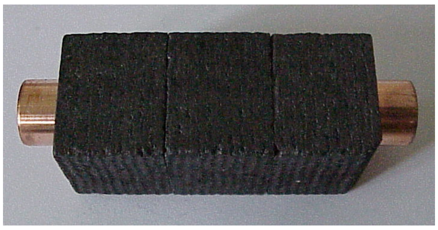


Fig. 11: Sepcarb® N11 monobloc

3.2 Properties of the Snecma Propulsion Solide materials

The properties of the material depend on texture and the matrix. For comparison, the characteristics of different materials are given in the next tables.

Mechanical characteristics:

Table 6: mechanical characteristics at RT

RT	Sepcarb® N11	Sepcarb® NB31	Sepcarb® NB41	Sepcarb® NS31
Density	1.75	1.9	1.9	2
Tensile stress X direction	38 MPa	130 MPa	150 MPa	160 MPa
Tensile stress Y direction	38 MPa	30 MPa	30 MPa	40 MPa
Tensile stress Z direction	27 MPa	10 MPa	9 MPa	25 MPa

The contribution of unbalanced texture appears clearly on these characteristics (table 6). The stress is about four times more in X direction than the others.

Thermal expansion characteristics:

Table 7: Coefficient of Thermal Expansion coefficient at 1000°C

1000°C	Sepcarb® N11	Sepcarb® NB31	Sepcarb® NS31
CTE X (10^{-6}/°C)	1.5	< 1	< 1
CTE Y (10^{-6}/°C)	1.5	< 2	< 2
CTE Z (10^{-6}/°C)	1.5	< 6	< 6

The Sepcarb® N11 shows a CTE homogenous in the three directions (table 7). It is not the case for NB31 and NS31.

Thermal characteristics:

Table 8: Thermal conductivity at room temperature

RT	Sepcarb® N11	Sepcarb® NB31	Sepcarb® NB41	Sepcarb® NS31
X (W / mK)	220	350	430	300
Y (W / mK)	220	120	120	100
Z (W / mK)	150	100	90	90

Table 9: Thermal conductivity at 1000°C

1000°C	Sepcarb® N11	Sepcarb® NB31	Sepcarb® NB41	Sepcarb® NS31
X (W / mK)	90	140	180	140
Y (W / mK)	85	50	50	50
Z (W / mK)	50	40	40	40

NB41, NB31 et NS31 show a high conductivity anisotropy due to a high fibers ratio and the fiber nature in one direction.
Introduction of ex-pitch fiber in the material allows to obtain higher characteristics as it can be observed with NB41 (tables 8-9). The conductivity is not penalized by Si doping.

The materials can also be improved to lower the erosion and the carbon release in the plasma.
In this way, coating the carbon / carbon with refractory materials appears clearly.

This is a challenging way that requires to be able to select and manufacture this kind of coating and especially to develop the intermediate layer system to accommodate the differential behavior between coating and substrate. Snecma Propulsion Solide is already involved in such new ways. In the field on aerospace applications, for example, ultra refractory compositions and coatings are experimented and could be used to improve the Snecma Propulsion Solide fusion composite materials.

4. CONCLUSION

During the fifteen last years, Snecma Propulsion Solide composite materials have been adapted and improved to follow the requirement and design evolutions of current and future Nuclear Fusion reactors.
In this area, Snecma Propulsion Solide has recently achieved several significant improvements on thermostructural composites:

- For SiC/SiC composite materials: new generation of Guipex®. This enhanced 3D reinforcement allows to reach high mechanical and thermal properties even in the thickness and to manufacture complex shape parts and tight parts.

- For C/C composite materials: newly developed NB41 Sepcarb®. This material owns increased thermal and mechanical properties. Furthermore, its simplified manufacturing process will allow mass production.

To deal with C/C erosion, new coating and refractory materials are in progress.

Nevertheless, a lot of works is still necessary to better match with the upgraded requirements of plasma facing components and blankets.

Improvements of fibers, textures, matrix, coatings are possible and must be considered in the future.

REFERENCES:

[1] Philippe E., International meeting on SiC/SiC Design and Material Issues for Fusion Systems, Oak ridge, Juanuary 18-19,2000.

[2] Bouillon E., Lamouroux F., Cavalier J.C. Spriet P. and Habarou G., An improved long life duration CMC for jet aircraft engine applications, ASME TURBO EXPO 2002, Amsterdam, The Netherlands, 2002, ASME ID GT-2002-30625.

[3] Bouillon E., Spriet P., Habarou G., Louchet C., Arnold T., Ojard G. ; C. Feindel D.T., Logan C.P., Rogers K., and Stetson D.P., Engine Test and Post Engine Test Characterization of self Sealing Ceramic Matrix Composites for Nozzles Applications in Gas Turbines, ASME TURBO EXPO 2004, power for Land, Sea and Air, Vienna Austria, 2004, ID GT-2004, ID GT-2004-53976.

[4] Bouillon E., Abbé F., Goujard S., Pestourie E., Habarou G., Mechanical and Thermal properties of self sealing matrix Composite and determination of the lifetime duration, Ceram. Eng. And Sci. Proc., 21, 3 2000, 459-467.

[5] Bouquet C. and al., Ceramic matrix composites cooled panel development for advanced propulsion systems" 45th-AIAA conf., April 2004, Palm Springs CA-USA.

[6] L. Filipuzzi, E. Subrenat, Thermostructural composites and nuclear fusion,. Industrial Ceramics volume 18 N.2 1998

[7] I. Berdoyes, J. Thebault,, Thermostructural composite materials: From space to advanced fission applications, EUROMAT 2005