Thermostructural composite materials: From space to advanced fission applications. EUROMAT 2005

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Abstract:

Materials improvement is one of the key factors for designing advanced solid rocket motor nozzles and for increasing missile vehicles performances. Those applications require materials with good resistance to high temperatures, to oxidant environments and to mechanical stresses.

Then, specific carbon-carbon composites materials have been developed for about thirty-five years at Snecma Propulsion Solide. Because of their strong thermal and mechanical performances, these composite materials are named at Snecma Propulsion Solide "thermostructural composite materials". The aim was to find replacement materials to tungsten, pyrographites and polycristallin graphites. Due to the extreme variety of carbon fibers, fibrous reinforcements and densification processes, these carbon/carbon composites materials, constitute a very wide range of materials, with mechanical and thermal characteristics depending on components and processes choice. The thermostructural C/C materials range is branded as Sepcarb®.

Because of the carbon-carbon sensibility to oxidation, ceramic matrix have been developed since the end of the seventies to substitute silicon carbide matrix for carbon matrix and perform long life materials withstanding high thermal fluxes and mechanical loads under oxidation environment. These thermostructural carbon/ silicon carbide composites materials are called Sepcarb-inox®. The other step is with ceramic fiber, and the material is called Cerasep®.

These composites, custom-made in accordance to technical requirements and working conditions, have found industrial applications, for example for engine flaps, thermal treatment facilities and experimental nuclear fusion reactors.

Snecma Propulsion Solide is equipped with facilities available to manufacture complex and large C-C or C/C-SiC components.

Moreover, Snecma Propulsion Solide has adequate competencies and software to design complete systems. Thus, Snecma propulsion Solide can be a partner involved in the definition of systems specifications.

These various topics will be successively approached and examples will be shown.

1. INTRODUCTION

The carbon-carbon thermostructural composites materials are considered as an attractive choice for plasma facing components in fusion application. These materials are low atomic number and they are of utmost importance for the thermal shocks resistance as well as heat resistance and high temperature strength.

Through its position as designer and manufacturer of propulsion systems, Snecma Propulsion Solide has pioneered and mastered the advanced technologies needed for the design, the development and production of carbon-carbon and ceramic composite materials.

Snecma Propulsion Solide (originally SEP), SAFRAN Group, devotes a continuous effort in this field, and is extending the prime application (space) to several others applications such as fusion and fission nuclear (industry) [1].

Development of carbon-carbon thermostructural composites materials started at SEP in 1969. In those days, the aim was to improve performances and reliability of solid propellant rocket nozzles and to find replacement materials to tungsten (too heavy), pyrographite (not suitable for making large integral parts) and polycrystalline graphites (too brittle).
For long duration use in oxidative environment Snecma Propulsion solid has developed Ceramic Matrix composites (CMC) since the mid 70's.

The acquired knowledge and know-how developed in solid propulsion applications turns to account for nuclear applications.

The matter of this paper is to present an overview of the composite materials manufactured at Snecma Propulsion Solide, their application in the nuclear field and the developments that could improve performances for fourth generation of fission reactors. The large range of thermostructural material properties allows to meet requirements of these applications [2].

2. OVERVIEW THERMOSTRUCTURAL MATERIALS AT SNECMA PROPULSION SOLIDE.

Snecma Propulsion Solide has developed thermostructural composite materials for a large range of aeronautic, space, defense and industrial applications.
These materials are called thermostructural composite materials because of both mechanical and thermal resistance.
The objectives of those thermostructural materials were:

- to withstand high temperatures (well above 1000°C),
- to obtain large parts with a greater toughness than monolithic ceramic or graphite which are vulnerable to thermal and mechanical shocks.
- to provide a more lightweight solution than refractory metals.

The material development is tuned according to the technical requirement.

2.1. Reinforcement:

Carbon-carbon composite materials can be considered as the first generation of thermostructural composites.
At the end of the seventies, SEP used to design solid rocket motors nozzles carbon-carbon materials with 2D reinforcement. But this kind of material suffers from poor isotropy and low shear resistance. Moreover, this reinforcement is sensitive to delamination especially for thick reinforcement. That is why SEP decided at the beginning of the eighty's to develop a 3D texture called Novoltex®. Novoltex® is a 3D carbon non-woven preform construction made through automatic technology from PolyAcriloNitrile fibers. This needling process consists in attaching fabric layers to each other's with carbon fibers pushed by hook fitted needles (Fig.1).

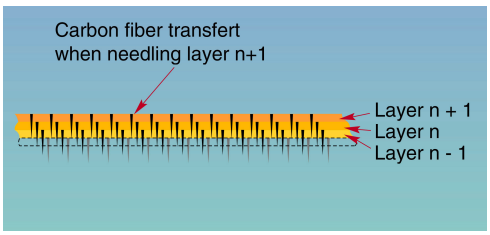


Fig.1: needle-punching Principe

To increase the performances and decrease the cost of Solid Rocket Nozzles materials, the development of that 3D reinforcement has been carried out.

New fabrics development has started at the end of the nineties. This needled 3D industrial fabric is called Multirex®. The last development step of this texture is a low cost 3D reinforcement called Naxeco® made from carbon fibers.

Snecma Propulsion Solide suggests a thermostructural composite material according to the required properties and working conditions. Then, the nature of the fibers (ex-PAN, ex-Pitch) their arrangement, the fabrics manufacturing and the densification processes are adapted.

For the ceramic-ceramics materials (Cerasep® range of materials), the preform is obtained by preparing a stack of SiC woven fabric layers. This stack is then compacted in a special tool so as to obtain a preform with a fiber volume fraction compatible with the procedure of gaseous processing of the silicon carbide matrix.
To avoid delamination risks, Snecma Propulsion Solide has also developed multiplayer weavines named Guipex®.

Preform production equipment

Snecma Propulsion Solide has set several needling equipments able to build preform flat panels up to 2.6m width by 6 m length, and cylindrical or conical parts up to 2.6 m diameter and 3m length.

The preform thickness is adapted to the final size of the parts.

The figure 2 shows the Snecma Propulsion Solide facilities.

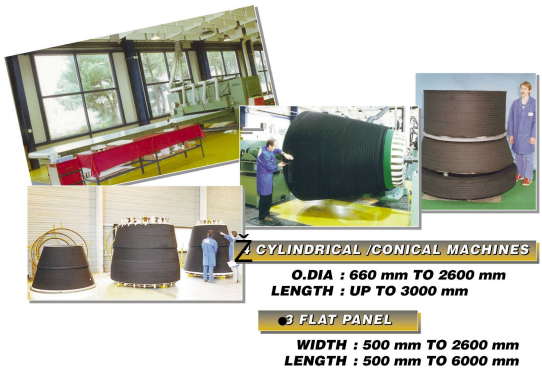


Fig.2: Novoltex® preforms manufacturing units

2.2. Densification:

High performances thermostructural composite materials imply different combinations of fibers, interphase layers and matrix. These three components give the composite materials their characteristics (density, thermal and mechanical properties).

Different processes can be used to densify the fibrous texture. Snecma Propulsion Solide is the only one European company that owns at the plant, the three densification processes. A schematic view is presented on the next chart (Fig.3).

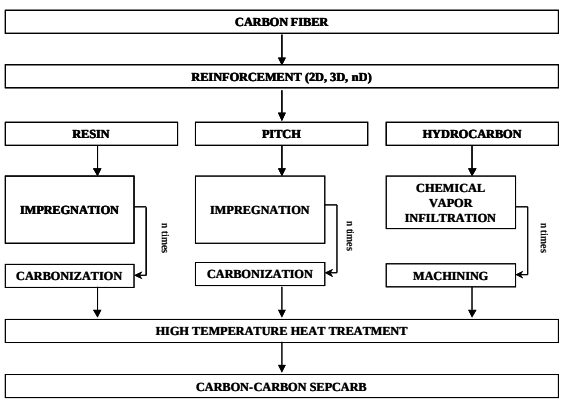


Fig.3: C/C manufacturing processes.

Note: The 3D reinforcement "Novoltex®" and "Naxeco®" are adapted to gas infiltration densification.

Carbon-carbon Matrix:

The matrix is obtained either by gas infiltration (CVI) or by pitch impregnation with carbonization.

Snecma Propulsion Solide has developed an optimized densification process with the aim of improving the reliability and reducing the cost.

Ceramic matrix:

For applications in an oxidative environment Snecma Propulsion Solide selects C-SiC or SiC-SiC composite materials. These materials are obtained by:

- Chemical Vapor Infiltration process (CVI),
- Densification with combination of liquid impregnation and hydrolysis (PIP).

Densification production equipment

Snecma Propulsion Solide owns many installations: CVI furnaces for both carbon and silicon carbide infiltration, resin impregnation units and pitch impregnation unit (Fig.4).

Specific developments have allowed to obtain carbonisation or CVI customized furnaces able to manufacture parts with 2.5m diameter and 3.5m length and sustain a temperature up to 3000°C.

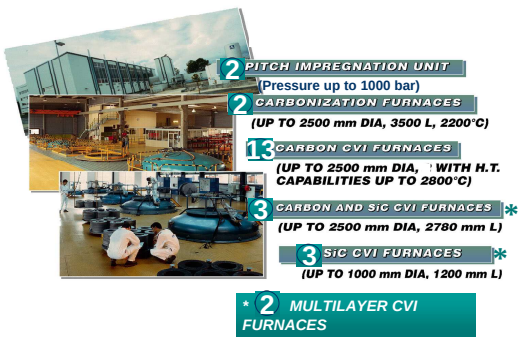


Fig.4: carbon and silicon carbide densification capabilities.

2.3. Comparison of 2D and 3D composite material:

The main characteristics of the 2D and 3D composite materials are compared in the next table (table 1):

	2D preform	3D preform
Mechanical properties		
Flexural bending	Good average bending but poor reliability for thickness greater than 100mm (local defect)	Good even for materials with thickness > 100mm
Thermal shock	Can be delaminated	Better
Interlaminar shear	Can be locally very low	Better
Thermal properties		
Conductivity	Good in the fiber direction Bad in perpendicular direction.	Not so good as 2D, but higher in Z direction
Expansion	Low in fiber direction High in Z direction	Low in all directions
Manufacturing	Industrial production experience	Industrial production experience

Table 1

So, mainly for carbon/carbon composite materials, Snecma Propulsion Solide prefers the 3D texture.

2.4. Selection of the densification process

According to the thermo-dynamical stability of the thermostructural material, Snecma Propulsion Solide chooses within its Sepcarb®, Sepcarb-inox® and Cerasep® range of materials, the most adapted for the applications. The choice of the composite material depends on working temperature, pressure, time exposition and chemical environment (Fig.5). Although the carbon-carbon and carbon-silicon carbide composite materials have both high temperature resistances, the environment will drive down the selection of the material.

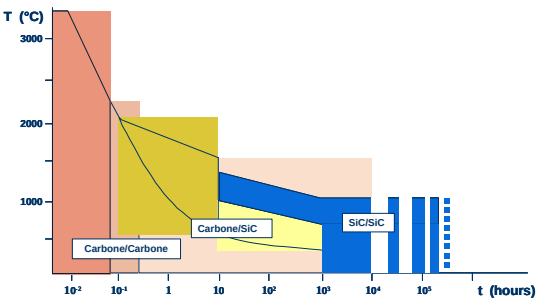


Fig.5: Domain of application of thermostructural composite materials

2.5. Example of main characteristics of materials

The properties of the material depend on texture, interphase and matrix. To give an idea, the characteristics of different materials are compared in the next tables. The characteristics are compared to graphite characteristics.

Mechanical characteristics:

	Graphite	C/C	C/C/SiC	SiC/SiC
Density	1.9	1.75	2.1	2.3
Tensile stress (MPa) In plane at RT	40	35 to 200	50 to 250	300
Tensile stress (MPa) In plane at 1000°C		55 to 250	60 to 300	300
Tensile modulus (GPa) In plane at RT	15	10 to 50	30 to 80	250

Table 2: mechanical characteristics

Composite materials are less brittle than graphite. The main characteristics depend on the nature of the fiber, the fiber ratio in the direction characterization and the matrix without forget the interphase (table 2).

Thermal expansion characteristics:

RT to 1000C	Graphite	C/C	C/C/SiC	SiC/SiC
CTE (10^{-6}/°C) In plane	5	2	2	4.5

Table 3: Coefficient of thermal expansion at 1000°C

Composite materials have a low thermal dilatation in the plane (table 3). The nature of the matrix impacts this characteristic.

Thermal characteristics:

RT	Graphite	C/C	C/C/SiC	SiC/SiC
Conductivity in plane at RT (W/m.K)	120	10 to 250	20 to 50	5 to 15

Table 4: Thermal conductivity at room temperature

The introduction of ex-pitch fiber in the C/C material allows obtaining higher characteristics (table 4).

By Si doping, the resistance to oxidative environment is well improved, and the thermal conductivity remains the same as for non-Si doped materials.

3. ADAPTATION OF THESE MATERIALS TO NUCLEAR FISSION APPLICATIONS

Direct outgrowths of work in Snecma Propulsion Solide laboratories, carbon-carbon, carbon-ceramic and ceramics-ceramics have found new industrial applications. Originally designed to meet the constraints of military rocket motor nozzles, these materials are today used in brakes, thermal furnaces, semiconductor equipments, experimental nuclear fusion reactors or other areas.

From the 2030 years, the fission reactors of fourth generation will be entered in service. In the new considered concepts, Snecma Propulsion Solide materials will interest two of them:

- Sepcarb® material is a good candidate for VHTR (Very High Temperature Reactor) concept,
- Cerasep® material will satisfy the technical need for GFR (Gas Fast Reactor) concept.

3.1. VHTR concept

For this application, new varieties of graphite have been developed in some locations and for specific purposes. This material will be replaced by carbon-carbon composite material, in particular, insulator and safety structure components like control rods.

Control rods are composed of several segments (Fig.6), which consist in two co-axial C/C tubes containing absorbent material. They have to be designed to withstand the distortion of the control rod channel. As a consequence, each section of the control rod is linked to the other with a carbon Fiber Composite pin, which allows the control rod to be flexible.
Due to their positions in the reactors, the control rods are facing neutron fluxes.

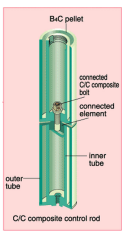


Fig.6: Schematic view of C/C composite control Rod [3]

The selection of Sepcarb® material depends on the requirements. The studies carried out for understanding the effects of irradiation on dimensional and mechanical properties of carbon-carbon composite material allow defining some characteristics of the material [4, 5, 6].

In fact, neutrons effects affect the dimensions and their variations depend on:

- Fiber nature: Ex-pitch fibers, because of their organization, are more stable after irradiation than ex-PAN fibers.
- Fiber architecture: the dimensional changes of 3D composite materials are more isotropic and lower than those of 1D or 2D composites.
- Heat treatment improves dimensional stability under irradiation.

Neutron also induces damages that lead to change the properties of CFC materials: mechanical properties and thermal conductivity.

So, some materials used in fusion nuclear like N11 or NB31 can be considered for this component.
But studies are in progress to develop a new material more isotropic at different scales. [7]

Another stress suffered by the material seems to be the oxidation in normal conditions and emergency. In this case, a coating will cover the material. Sepcarb-inox®, like NS 31, developed for the fusion nuclear can meet these requirements.

3.2. GFR concept

In opposite to VHTR concept, GFR concept cannot be defined with carbon-carbon material because of the high-speed neutrons.

The SiC-SiC materials produced by Snecma Propulsion Solide for Fusion nuclear applications (Cerasep®) offer a potential solution. Cerasep® combine a number of attractive properties: low activation, good resistance to shocks and heat cycling, convenient strength and an ability to retain their good mechanical properties to temperatures over 1 000°C.

Three materials in the range of SiC/SiC composite materials (Cerasep® brand) have been developed for nuclear fusion:

- A standard SiC-SiC composite material. CERASEP® N2-1 was used to carry out the initial evaluation work and demonstrate the various benefits offered by these materials for fusion application. One of the characteristics of this particular SiC-SiC material composite was

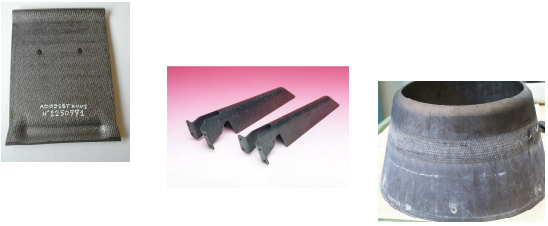
its two-dimensional strengthening feature. This performance is achieved using standard fiber (a fiber containing oxygen) and by increasing the density of the composite part by CVI.

- CERASEP® N3-1 was subsequently developed in order to improve the material's shear-related properties and to reduce the macro-porosities. This material is also produced using standard fibre, however this grade offers an innovative three-dimensional strengthening feature, named Guipex®.
- CERASEP® N4-1. This material is performed with a more stable fiber.

The main advantages of 3-D material over the 2-D material are as follows:

- Thermal conductivity in the Z-direction is increased,
- Interlaminar shear failure stress is increased.

Snecma Propulsion Solide has experienced to manufacture simple geometry parts, like plate or cylindrical part, and also complex parts. Examples



of complex parts are given in the figure 7.

Fig.7: examples of complex parts

But these Cerasep® N2-1 and N3-1 materials have some limitations, mainly due to the impurities of the fiber and a insufficient conductivity in Z direction.

Further improvements have been identified. Particularly, it is important to:

- Use new, improved-purity SiC fibers (virtually stoechiometric and "oxygen-free"). The thermal conductivity of such fibers is intrinsically higher than that of the standard fiber. Moreover, the rate at which its properties change when exposed to neutron irradiation will be reduced. Other positive aspects relating to the use of these fibers are:
  * an increase in the maximum service temperature, from 1100°C to about around 1400°C.
  * a significant improvement in mechanical properties.
- Develop specific dedicated textures, adapted to the design of the parts to be manufactured. One way is to perform 3D reinforcement like for Sepcarb® materials.
- Adapt the fiber/ matrix interface to reduce the amount of carbon and thus the irradiation behaviour will be improved.
- Adapt the matrix production processes with the aim of increasing the thermal conductivity of the materials.

4. CONCLUSION

Snecma Propulsion Solide has developed a large range of carbon-carbon, carbon-silicon carbide and SiC-SiC composite materials with high mechanical and thermal performances.
SAFRAN Group manufactures over 400 metric tons per year of C-C, C-SiC and SiC-SiC composites materials, mainly for solid rocket propulsion, brakes discs, jet engines and fusion nuclear applications.
Development of composite initially dedicated to rocket engine nozzle application and since the beginning of the years 90 for fusion nuclear, is now expending its scope of activities for fission application.
For this specific application existing composites materials must be adapted. And the ways to improve those Snecma Propulsion Solide composite materials are identified.

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