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# Materials design and processing of high temperature ceramic matrix composites: state of the art and future trends

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# Materials design and processing of high temperature ceramic matrix composites: state of the art and future trends

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**Abstract**—The material design of ceramic matrix composites (CMCs) is discussed in terms of fiber nature and architecture, interphases (pyrocarbon, BN, multilayers), matrices and seal-coating, taking into account lifetime considerations. CMCs are processed by liquid or gas phase routes. Besides the well established processing routes, such as polymer impregnation and pyrolysis (PIP), slurry impregnation/hot pressing (SIHP) and isothermal/isobaric chemical vapor infiltration (I-CVI) techniques, emerging processes allowing densification times of the order of a day, are discussed.

*Keywords*: CMC; C/C; SiC/SiC; design; interphase; processing.

## 1. INTRODUCTION

The ceramic matrix composites (CMCs) considered here consist of continuous (or semi-continuous) ceramic fibers embedded in a ceramic matrix, such as carbon, silicon carbide, silicon nitride or a refractory oxide. They are usually designed for applications in severe environments. It is now well established that CMCs are tough materials when the fiber–matrix (FM) bonding is properly controlled during processing, i.e. through the use of a thin layer of a compliant material with a low shear strength, referred to as the interphase. It has been recently suggested that the best interphase materials might be those with a layered crystal structure, e.g. pyrocarbon, or with a layered microstructure, such as $(PyC-SiC)_n$ multilayers [1].

The design of a CMC, in terms of materials, is dictated by the nature of the application. It usually includes: (i) the choice of a proper fiber and fiber architecture; (ii) the selection of suitable interphase and matrix materials and, when necessary; (iii) the use of an external seal coating. As the composition of the CMC is fixed, a processing technique has to be selected on the basis of several considerations, including the size and shape of the part as well as the number of parts to be produced. Because ceramic remains brittle within a broad range of temperature, CMCs should be fabricated according to processes that do not damage the fibers, which generally means pressureless techniques and use of matrix precursors. Further, in order to avoid strong chemical reactions between the constituents or detrimental change in the fiber microstructure, low temperature processing techniques are often preferred. The starting material can be a simple continuous fiber tow (or tape), fiber fabrics or, more often, a multidirectional *n*D-fiber preform. The interphase material is classically deposited on the fiber surface by chemical vapor deposition (CVD) or infiltration (CVI). Then the fiber architecture is densified according to liquid or gas phase routes, or a combination of both (hybrid processes) [2].

## 2. MATERIALS DESIGN

### 2.1. Fiber architecture

In the field of CMCs, *carbon fibers* are by far the most attractive reinforcements. Carbon is one of the most refractory materials and one of the very few materials whose mechanical properties increase as temperature is raised. Further, a variety of carbon fibers are available, some of them being relatively cheap. Unfortunately, carbon reacts with oxygen at temperatures as low as 400–500°C, with formation of gaseous oxides (active oxidation). As a result, the use of carbon fibers in CMCs that will be exposed to oxidizing atmospheres, demands internal/external oxidation protection. Hence, *non-oxide fibers*, such as silicon carbide or related fibers, known to undergo passive oxidation with formation of a protective silica scale are more appropriate. During many years, the SiC-based fibers available on the market, such as the Si–C–O Nicalon fibers (from Nippon Carbon) or the Si–C–O (Ti) Tyranno fibers from Ube Industries, were limited in thermal stability, undergoing decomposition at 1100–1200°C [3–11]. As a result, their use was limited to low temperature processing techniques and applications. Modern oxygen-free fibers with a stoichiometry close to C/Si (at) = 1 and displaying a much higher thermal stability (Hi-Nicalon S from Nippon Carbon, Tyranno (SA) from Ube Industries or Sylramic from Dow Corning) are now available [12–17]. Such fibers might become attractive for CMCs if their cost is reduced significantly. Finally, refractory *oxide fibers* would be the best reinforcements for CMCs used in a prolonged manner at high temperature in oxidizing atmospheres. These fibers actually exist on the market, as pure alumina (Nextel 610 from 3M) or as mixed alumina-mullite (Nextel 720 also from 3M) fibers, but their high temperature mechanical properties are relatively poor beyond 1000–1100°C due to grain growth and creep [18–23].

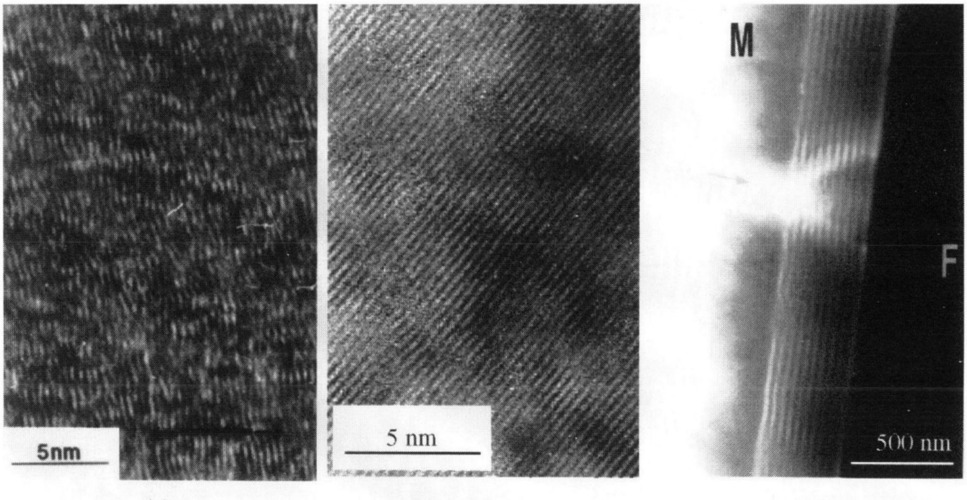
Ceramic yarn fibers are sometimes employed as continuous *single tows*. After impregnation with a liquid precursor of the matrix and winding, they yield a prepreg-type or semi-product material, which is used to produce laminates according to techniques similar to those developed for their polymer matrix counterparts. However, ceramic fibers are more generally employed as self-standing multidirectional *preforms*, fabricated by weaving processes. Such *n*D-fiber architectures are well suited to rapid processing techniques and complex loading schemes [24, 25].

## 2.2. *Interphase materials*

In most CMCs, an interphase is used to control the FM-bonding during processing. It is a key constituent with several functions, including FM load transfer, matrix microcrack deflection (the so-called fuse function) and diffusion barrier (in reactive FM systems). The design of the FM-interfacial zone in a given CMC for a given application is somewhat difficult, and it is rarely performed in an optimized manner. The best interphase materials might be those with a layered structure or microstructure, the layers being parallel to the fiber surface and weakly bonded to one another, and the whole interphase strongly adherent to the fiber [1, 26]. The most commonly employed interphase consists of a thin layer (less than 1 $\mu$m) of anisotropic pyrocarbon deposited on the fiber surface by CVD/CVI from a suitable hydrocarbon (Fig. 1a).

Pyrocarbon is an excellent interphase material from a mechanical standpoint. However, it is oxidation prone. The oxidation of carbon starts at about 450°C. It occurs with formation of gaseous species exclusively (CO or/and $CO_2$) and hence with a weight loss, the material being progressively consumed (active oxidation). It is also anisotropic and strongly depending on the occurrence of specific impurities (such as alkali or alkaline earth cations) often present in carbonaceous materials.

When used in a SiC/SiC composite exposed to an oxidizing atmosphere under cyclic loading, a pyrocarbon interphase can be consumed with a dramatic change in the FM interfacial bonding and hence in the overall mechanical behavior of the com-



(a) (b) (c)

**Figure 1.** Interphases in SiC/SiC composites: (a) anisotropic pyrocarbon; (b) hex-BN; and (c) $(PyC-SiC)_{10}$ multilayers according to [73], [31], and [33], respectively.

posite. Under such conditions, interphases with an improved oxidation resistance should be employed. A first approach is to select a material displaying intrinsically a high oxidation resistance, ideally a layered refractory oxide compatible with both the fiber and the matrix. Indeed, the number of such oxide interphases is extremely limited. Known examples are magnetoplumbite-type oxides, e.g. hibonite ($CaAl_{12}O_{19}$), or mica-type oxides such as fluorophlogopite $KMg_3$ $(SiAl)O_{10}F_2$ or related phyllosiloxides $(KMg_2Al(Si_4)O_{12}$ [26–29]. Moreover, the deposition of a layered oxide thin film with a controlled microtexture (the layers being parallel to the fiber surface) by sol-gel or CVD/CVI techniques, is not straightforward. The thermal stability of layered oxides at high temperatures is often limited, which is typically the case for micas and related materials. Another potential interphase material is hexagonal BN which has a layered crystal structure similar to that of graphite but whose oxidation starts at about 850°C and is passive (formation of condensed $B_2O_3$) [30]. Hex-BN can be deposited by CVD/CVI from a variety of gaseous precursors, the most commonly used being $BX_3$–$NH_3$ mixtures (with $X = F, Cl$). It is often turbostratic (as its pyrocarbon counterpart) and even amorphous, depending on the nature of the precursor and the T–P conditions. Highly ordered hex-BN has been deposited at low temperatures from $BF_3$–$NH_3$ but under conditions which are aggressive for SiC-based fibers (Fig. 1b) [31]. However, hex-BN is sensitive to moisture when poorly crystallized [32]. A second approach is to design *self-healing* multilayered $(X-Y)_n$ interphases, combining at a nm-scale a compliant $X$ material such as pyrocarbon with a stiff glass-former $Y$, such as SiC (Fig. 1c), the formation of the glass at a high enough temperature, protecting the mechanical fuse against oxidation [26, 33]. The concept can even be extended to $X-Y$ sequences in which the mechanical fuse is a glass-former itself, an example being the recently proposed $(BN-SiC)_n$ multilayered interphases [34]. Finally, in a few CMCs, such as the C/C composites, an interphase is not used, the mechanical fuse being the FM interface itself which has been weakened enough by, for example, thermal treatment at very high temperature.

### 2.3. Matrix and seal-coating

Ceramic matrices also fall into two categories, namely the *non-oxide* and the *oxide matrices*. Among the first family, the *carbon matrix* (associated with carbon fibers) is the most commonly used material on the basis of cost, processing and properties considerations. C/C are by far the most developed CMCs and the only materials used in volume production. The carbon matrix can be formed either from liquid or gaseous precursors, with a variety of microtextures and hence a variety of properties [35, 36]. Isotropic carbon displays low mechanical characteristics. Highly anisotropic carbons, such as those deposited by CVD/CVI with the so-called rough laminar (RL) microtexture, exhibit after a graphitization treatment beyond 2000°C, a high thermal conductivity.

The advantage of *SiC* and *$Si_3N_4$ matrices* lies in their oxidation resistance (they are protected by a silica scale up to 1500–1600°C). However, most CMCs are

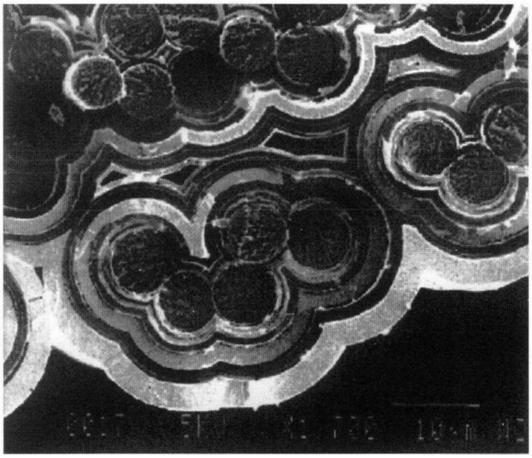


Figure 2. Model composites with self-healing multilayered matrix, reinforced with carbon fibers, according to [39].

inverse composites ($\varepsilon_m^R < \varepsilon_f^R$), and the matrix undergoes microcracking when loaded at a high enough stress level, e.g. in cyclic loading. As a result, oxygen can diffuse via the matrix microcracks and reach the oxidation-prone interphases and fibers [37]. To impede or slow down the in-depth diffusion of oxygen, the concept of multilayered ceramics has been extended to the matrix [38]. An example of a composite with a *self-healing* matrix reinforced with carbon fibers, has recently been reported by Lamouroux *et al.* (Fig. 2) [39]. The multilayered matrix comprises mechanical fuse layers arresting the cracks and glass former layers entrapping oxygen in a low viscosity glass.

A variety of *oxide matrices*, such as alumina, mullite, stabilized zirconia or silica-based glass-ceramics can also be considered. Glass-ceramics, such as those from the $Li_2O-Al_2O_3-SiO_2$ (LAS), $CaO-Al_2O_3-SiO_2$ (CAS) or $BaO-MgO-Al_2O_3-SiO_2$ (BMAS) systems, have been extensively studied. One of the advantages of such glass–ceramic matrices lies in the fact that they are used in their low viscosity state (beyond $T_g$) to embed the fibers and then ceramed to increase their refractoriness [40].

Finally, non-oxide CMCs often receive a *seal-coating* to seal the open residual porosity and hence to impede the in-depth diffusion of oxygen. A variety of seal-coatings has been suggested, including a single layer of a glass-former such as SiC or multilayered smart coatings [41]. In the specific case of C/C composites, the oxidation protection usually comprises both inhibiting particles dispersed within the matrix and a complex external seal-coating [42, 43].

## 3. PROCESSING

CMCs are fabricated via liquid or gas phase routes, from fiber tows, fabrics or *n*D-preforms. Low temperature, pressureless, near net shape processes are preferred in order not to damage the fibers and to reduce the cost. The choice of a given processing technique is dictated by the size, the shape and the number of parts to be produced.

### *3.1. Liquid phase routes*

*3.1.1. Reactive melt infiltration (RMI).* RMI processes can be used when one of the elements of the matrix has a low (or relatively low) melting point and readily wets the fiber preform. In the DIMOX process (Lanxide), the molten element such as an aluminum alloy (mp $\approx$ 650°C), reacts with the atmosphere, e.g. the air, as it climbs by capillary forces in the fiber preform pore network, yielding an alumina matrix composite [44–47]. The alumina matrix grows in the fiber preform open pore network, from the molten alloy, according to a complex dissolution (of oxygen)/precipitation (of alumina) process, in which Mg (present in the alloy) plays a key role. A layer of MgO (permeable to oxygen diffusion) formed at the liquid metal surface as the result of the oxidation of Mg, prevents the formation of a dense protective scale of alumina that would stop the in-depth diffusion of oxygen. With a processing temperature $\approx$ 1200°C, a variety of fibers including Nicalon-type fibers, can be utilized (Fig. 3). In the SILCOMP process (General Electric), a ceramic fiber preform which has been first consolidated with carbon, is impregnated with liquid silicon at $\approx$ 1450°C. Liquid silicon readily reacts with carbon to yield a SiC-based matrix. In this latter process, only fibers with a high thermal stability, such as carbon or Hi–Nicalon-type fibers, can be used [48–52]. Furthermore, as both liquid aluminum and liquid silicon are very corrosive, the fibers have to be protected. Dual BN–SiC coatings, BN being the mechanical fuse and SiC a diffusion barrier, have been successfully used in Nicalon/$Al_2O_3$ and Hi–Nicalon/SiC composites [53]. Some residual Al or Si is usually present in the matrix, but this can be removed by wicking (Al) or entrapped in the matrix as refractory silicide (Si), when necessary. Both processes yield near net-shape composites.

*3.1.2. Polymer impregnation and pyrolysis (PIP).* In the PIP-process, a fiber preform is impregnated with a liquid thermosetting organic (or organometallic) precursor of the matrix. After curing, the material is pyrolyzed, a weight loss and

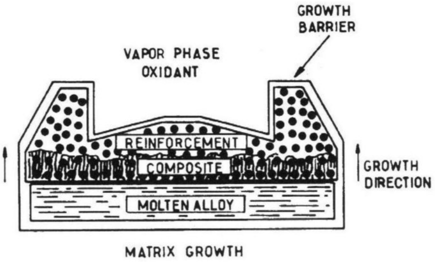


**Figure 3.** Fabrication of a near net shape alumina matrix composite by the DIMOX process (schematic), according to [44].

shrinkage of the matrix occurring during the pyrolysis [54–57]. This important drawback can be overcome by loading the precursor with an inert filler (such as a fine powder of the matrix) or/and by repeating several times ($n = 6$ to 10) the impregnation/curing/pyrolysis sequence (hence increasing the processing time and labour cost). Conversely, this process relies on simple technology.

*3.1.3. Slurry impregnation and hot pressing (SIHP).* The SIHP-process can be used to fabricate a variety of CMCs. In a first step, a fiber tow (or tape) is impregnated with a slurry, i.e. a stable suspension of the matrix in a liquid containing a fugitive binder and various additives, and taken up on a drum, yielding after drying a *prepreg*-type material. After cutting and stacking, the prepreg layer assembly is hot-pressed in order to yield a dense matrix composite [40]. Two important requirements should be fulfilled. First, the fibers should be stable under the hot pressing conditions, limiting the choice to the HM–carbon fibers and Hi–Nicalon-type fibers. Second, the matrix should soften and flow during hot-pressing, which is typically the case for glass–ceramic matrices, as already mentioned, the hot-pressing temperature being 1200–1400°C. Conversely, sintering additives have to be added to the slurry, for refractory non-oxide matrices, such as SiC or $Si_3N_4$, hot pressing being performed at much higher temperatures (up to 1700–1800°C, for SiC), with some risk of fiber degradation [58–61].

### *3.2. Gas phase routes*

In the gas phase routes, referred to as *chemical vapor infiltration* (CVI), the matrix is formed within the preform pore network, from a gaseous precursor, e.g. a hydrocarbon for carbon. CVI-processes involve mass transfer of reactants and products in the porous medium and homogeneous/heterogeneous reactions (Fig. 4). An important requirement to achieve a high degree of densification, is that the pore network remains open. CVD/CVI processes yield ceramic deposits of high quality from a structural and mechanical standpoint.

*3.2.1. Isothermal/isobaric CVI (I-CVI).* In I-CVI, the reactant/product mass transfers in the preform are mainly by diffusion. In order to favor *in-depth* deposition, the process has to be conducted at low temperature (800–1000°C) and low pressure (a few kPa or 10 kPa) to lower the reaction kinetics and enhance the mean free paths of the molecules in the porous preform, which hence poses advantages and drawbacks [62]. A variety of fibers can be used, even those of relatively low thermal stability, such as Nicalon-type or transition alumina fibers. The fibers are not damaged as long as they are chemically compatible with the gas phase. The process is highly flexible but relatively slow, i.e. a large number of preforms (eventually of different sizes and shapes) can be treated simultaneously. The composites usually display some residual porosity and a density gradient. I-CVI can be used to deposit a variety of interphase and matrix materials (non-

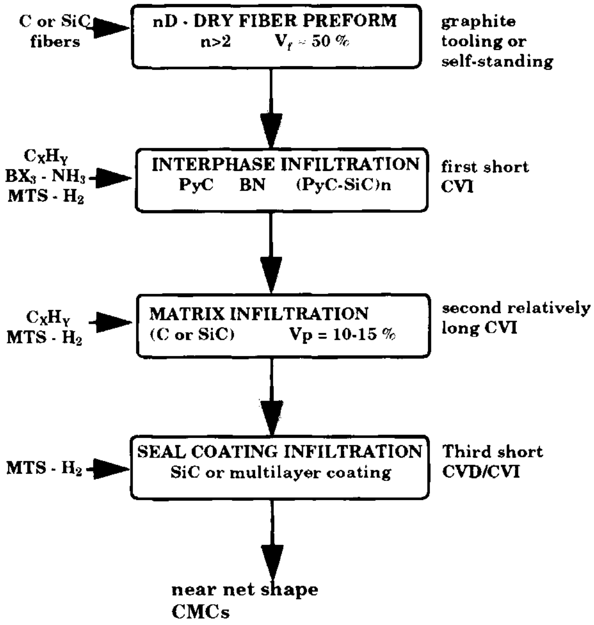


**Figure 4.** Fabrication of near net shape non-oxide composites (C/C; C/SiC; SiC/SiC and related materials) by CVI (schematic flow chart).

oxides or oxides) [35, 63]. It has been transferred to the plant level for the production of C/C, C/SiC and SiC/SiC composites.

*3.2.2. Rapid CVI process.* The densification rate can be significantly improved, when mass transfer in the preform occurs by fast convection (instead of slow diffusion) and the temperature is raised. This is usually achieved by applying a temperature gradient (TG-CVI) or/and a pressure gradient (F-CVI) to the preform. Unfortunately, these improved CVI-techniques are less flexible than I-CVI [64–70].

*3.2.3. Pressure-pulsed CVI (P-CVI).* In P-CVI, reactants and products are respectively injected in the reactor and removed by pumping, in a periodic manner. When the duration of each pulse is short enough, i.e. of the order of a second, the deposit can be built almost atomic layer by atomic layer [71–73]. Further, if the nature of the precursor is periodically changed, multilayered ceramics where the elementary layer thickness can be of the order of a few nm, can be deposited in a porous preform. $(PyC{-}SiC)_n$ or $(BN{-}SiC)_n$ interphases, as well as self-healing matrices have been produced by P-CVI in SiC (or C) fiber composites to increase the lifetime in oxidizing atmospheres (Figs 1c, 2, 5) [33, 34, 74]. Hence, the P-CVD/CVI is a powerful tool to engineer multilayered ceramics at different scales (ranging from the nm- to the $\mu$m-scales). As an example, it has been shown that P-CVD/CVI can be used to fabricate $(PyC{-}SiC)_n$ multilayered ceramics mimicking the layered structure of nacre in seashells [75].

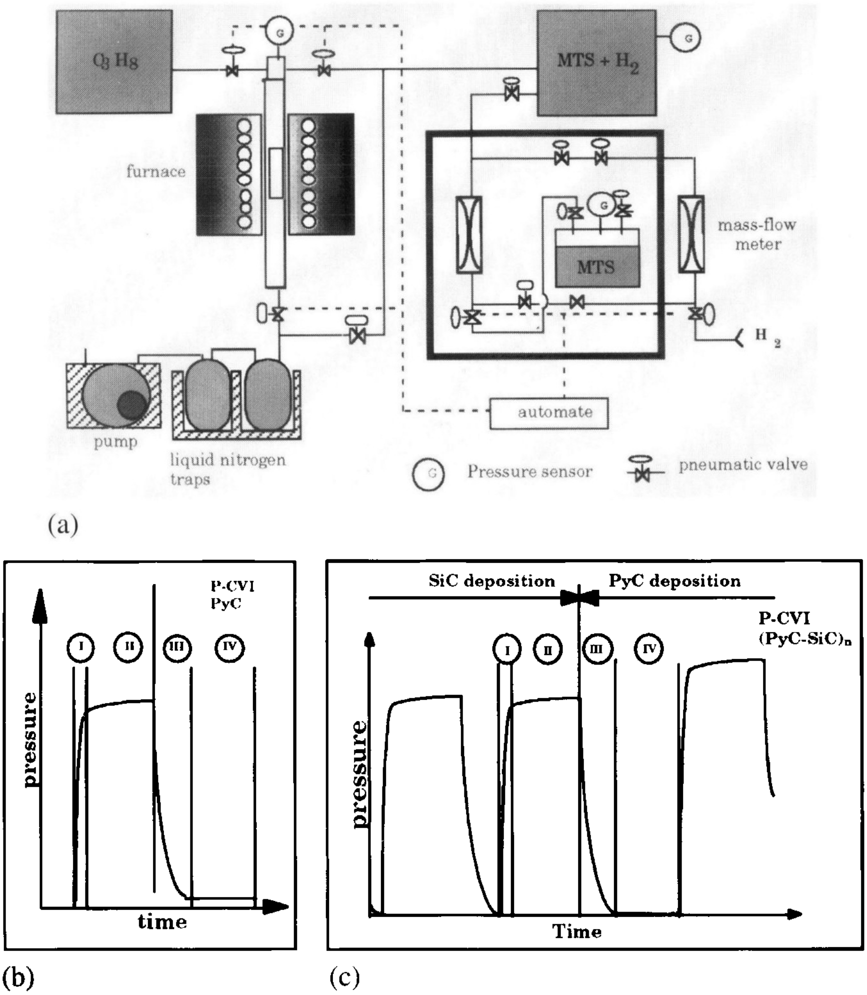


**Figure 5.** Apparatus for the fabrication of multilayered $(PyC-SiC)_n$ ceramics at the laboratory scale (schematic): (a) experimental set-up; (b) pressure pulse for a homogeneous deposit; (c) pressure pulses for the deposition of the (PyC–SiC) elementary sequence, according to [33].

*3.2.4. Film boiling process (FBP).* In FBP (CEA, Textron), the fiber preform is directly immersed in a boiling liquid precursor, such as cyclohexane for carbon, and heated to 1100–1200°C by induction with a susceptor. The extremely high densification rates which have been reported result from the high deposition temperature and reactants/products mass transfers [76–78].

## 4. CONCLUSION

The material design of CMCs relies upon available *ceramic fibers* and supposes an optimization of both the fiber/matrix interfacial zone and the matrix itself. Some progress has been achieved in the field of ceramic fibers. Quasi-stoichiometric SiC fibers display a higher thermal stability than the Si–C–O fibers. Hence, they are compatible with high temperature processing techniques. However, their cost is too high and their stiffness (≈ 400 GPa) might be a problem for the fabrication of *n*D-preforms. Si–B–C–N fibers, thermally stable and creep resistant, also appear to be attractive materials.

The key point in terms of material design is probably to improve the *lifetime* of CMCs in oxidizing atmospheres, via innovative interphase and matrix materials and concepts. A first approach has been to replace the carbon interphase by less oxidation prone materials. However, the most promising of them, BN, is usually moisture sensitive when deposited at low temperatures. A second approach has been the use of multilayered interphases. Its success lies in the fact that such interphases can be widely tailored, permitting the decoupling of some of the contradictory interphase functions. The extension of this approach to the matrix itself also appears promising, at least when applied to composites processed via CVI-processes.

In terms of processing, *rapid densification* techniques with processing times of the order of the day, are emerging beside well established routes (I-CVI, PIP, SIHP techniques) which could still be improved. Even if they display less flexibility, they may be appropriate for specific matrix compositions (the DIMOX process for alumina or the SILCOMP process for SiC) or specific applications.

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