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## FIBER-REINFORCED CERAMIC MATRIX COMPOSITES: STATE OF THE ART, CHALLENGE AND PERSPECTIVE

(ARTYKUŁ ZAMAWIANY)

Ceramic matrix composites (CMCs) are non-brittle structural ceramics for application at high temperatures. They consist of ceramic fibers embedded in a ceramic matrix, the fiber/matrix bonding being controlled through weak enough interphase. CMCs are processed following gas, liquid or powder routes. Their main properties are presented and discussed, including mechanical behavior, thermal conductivity, dimensional stability, friction and the effects of an oxidizing atmosphere or nuclear radiations. Finally, the applications of CMCs are briefly presented in rocket motors, spacecraft thermal protection, aerojet engines and cogeneration gas turbines, braking systems and high temperature nuclear reactors.

**Key words:** ceramic matrix composites, C/SiC, SiC/SiC, HT-applications

### KOMPOZYTY CERAMICZNE WZMACNIANE WŁÓKNAMI: STAN BADAŃ, WYZWANIA I PERSPEKTYWY

Kompozyty o osnowie ceramicznej (CMCs) są niekruchymi konstrukcyjnymi materiałami ceramicznymi stosowanymi w wysokich temperaturach. Składają się z włókien ceramicznych otoczonych ceramiczną osnową, przy czym o wiązaniu włókien z osnową decyduje odpowiednio słaba faza pośrednia. Kompozyty te wytwarza się metodami wykorzystującymi fazę gazową, fazę ciekłą albo technologie proszkowe. Zaprezentowano i omówiono ich podstawowe właściwości, do których należą właściwości mechaniczne, przewodność cieplna, stabilność wymiarowa, tarcie i wpływ atmosfery utleniającej oraz promieniowania jądrowego. Na koniec przedstawiono pokrótce zastosowania CMCs w silnikach rakietowych, osłonach termicznych statków kosmicznych, silnikach odrzutowych i turbinach gazowych, w układach hamulcowych i w wysokotemperaturowych reaktorach jądrowych.

**Słowa kluczowe:** kompozyty o osnowie ceramicznej, C/SiC, SiC/SiC, zastosowania w wysokich temperaturach

## INTRODUCTION

Ceramics often display high melting point, stiffness, hardness, low density and corrosion resistance. Conversely, they are intrinsically brittle and poorly reliable under load. The mechanical properties of ceramics can be significantly improved in terms of toughness, shock resistance and reliability through the use of the concept of fiber reinforcement which has led to a new class of materials referred to as ceramic matrix composites or CMCs [1-4].

CMCs are ceramic materials consisting of ceramic fibers, oriented unidirectionally or arranged in nD architectures (with  $n = 2, 3, 4 \dots$ ) and which are embedded in a ceramic matrix of same or different chemical composition (such as C/C, C/SiC, SiC/SiC,  $Al_2O_3/Al_2O_3$  with the fibers named first). One of the keys for achieving improved mechanical properties is a proper control of the fiber/matrix (FM) bonding which should not be too strong nor too weak. An important breakthrough has been the discovery that the FM-bonding could be controlled via the use of a compliant fiber coating with a low shear strength referred to as the interphase, the most commonly

used in non-oxide CMCs being pyrocarbon (PyC) [5, 6]. CMCs with such an interphase display a non-linear stress-strain tensile behavior and fail in a non catastrophic manner, which are outstanding features for ceramics [7, 8]. Presently, the best ceramic reinforcements in terms of strength and creep resistance are non-oxide fibers (carbon and SiC fibers). Hence, the most commonly employed CMCs are C/C, C/SiC and SiC/SiC. Since these composites are usually exposed to corrosive atmospheres at high temperatures, a key issue is the long-term behavior and lifetime of these materials [9, 10].

The aim of this contribution is to give an overview of the potential, challenge and perspective of CMCs for application in aerojet engines, gas turbines and nuclear reactors.

## CMC-PROCESSING

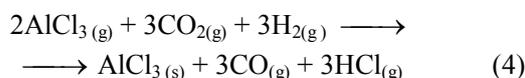
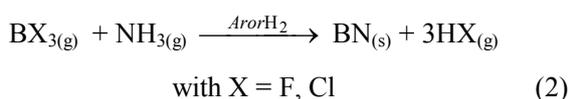
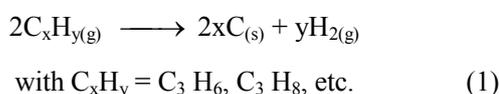
The processing of CMCs usually includes three steps: (i) the deposition of the interphase, (ii) the infiltration of

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the matrix in the fiber architecture and (iii) the deposition of a seal-coating (referred to as an environmental barrier coating (EBC)) on the external surface of the composite to improve the corrosion resistance. Since the ceramic fibers are brittle and often of limited stability, all these steps require mild temperature/pressure (T, P) conditions. This can be achieved following three different routes, each having advantages and drawbacks.

### Gas phase route

In the gas phase route, or chemical vapor infiltration (CVI) process, the interphase, matrix and even the EBC are successively deposited from appropriate gaseous precursors, under reduced pressure and at moderate temperature (typically, 900÷1100°C), according to the following overall equations [11, 12]:



Equations (1) and (2) correspond to the deposition of PyC and BN interphases whereas equations (3) and (4) are related to the infiltration of SiC and alumina matrices.

The CVI-process displays several advantages (Fig. 1a). Firstly, it is a low T, P - process which can be utilized even with ceramic fibers of limited thermal stability. Secondly, it yields deposits of high microstructural quality and whose composition can be tailored by adjusting the nature of the precursor and the deposition parameters. As an example, SiC-based matrix can be deposited, from  $CH_3SiCl_3$  (MTS)- $H_2$ , as pure  $\beta$ -SiC, SiC + Si or SiC + C mixtures. Further, the deposit can be almost amorphous, crystalline and highly textured, or consisting of engineered multilayers (when utilizing pressure pulsed CVI (P-CVI)) [13]. Thirdly, the CVI-process when conducted under isothermal-isobaric conditions (I-CVI) is a highly flexible technique which can be used to coat individual fibers in a fiber tow, to densify a nD-preform, or to treat simultaneously a large number of preforms with different sizes and shapes. Finally, CVI is a near net shape approach to CMC-processing. The CVI-process also displays a few drawbacks. Firstly, it yields composites with some residual open porosity typically  $V_p \leq 10\div 15\%$ . Such a porosity

decreases significantly their thermal conductivity and favors the effect of corrosive environments. Secondly, I-CVI is a relatively slow technique. It has to be conducted under low T, P conditions to favor in-depth deposition (densification) and to avoid an early sealing of the fiber architecture porosity.

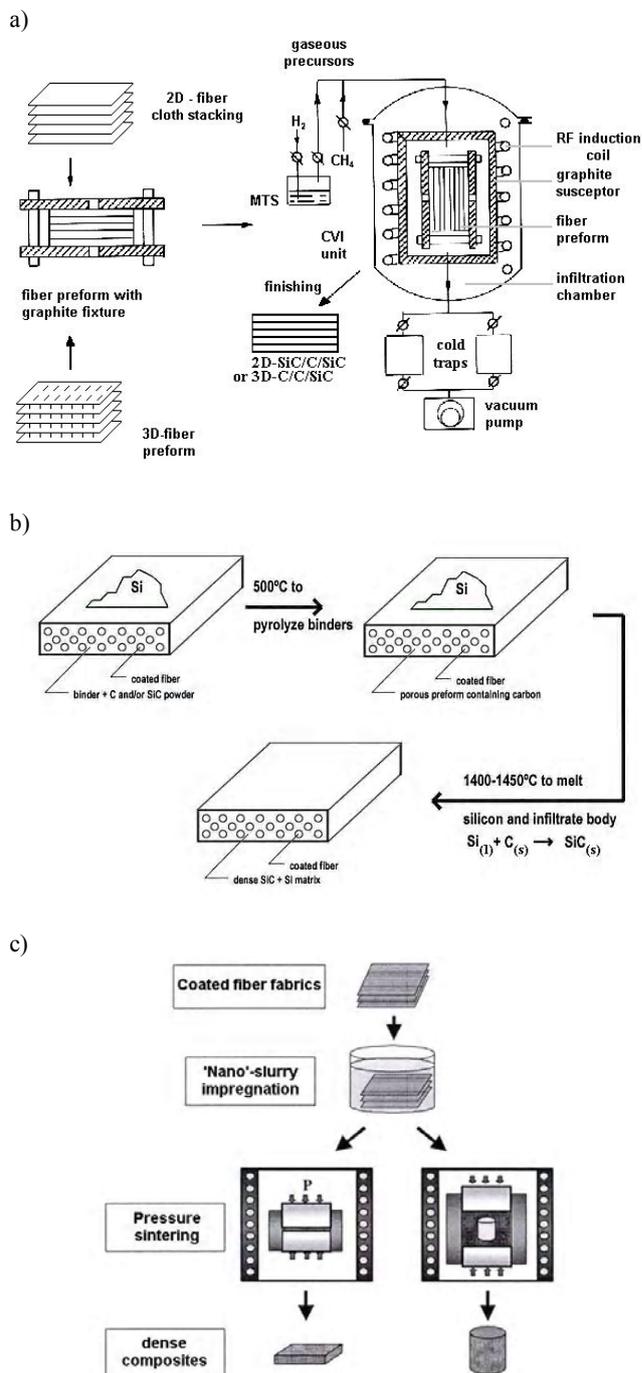


Fig. 1. Processing routes to ceramic matrix composites (schematic): a) I-CVI-process for C/SiC and SiC/SiC composites, b) RMI-process for SiC-matrix composites (according to ref. [25]) and c) NITE/SIHP process for SiC/SiC composites (according to [33])

Rys. 1. Metody wytwarzania kompozytów o osnowie ceramicznej (schemat): a) izotermiczno-izobaryczny proces infiltracji fazą gazową (I-CVI) dla kompozytów C/SiC i SiC/SiC, b) proces infiltracji cieczą reaktywną (RMI) dla kompozytu o osnowie SiC [25], c) procesy NITE (infiltracji nanoprošków i nietrwałej fazy eutektycznej) oraz

SIHP (impregnacji zawiesiną i prasowania na gorąco) dla kompozytów SiC/SiC [33]

As a consequence, the deposition rate is low and the time necessary to fully densify a given preform can be relatively long. However, densification can be achieved in a much shorter time (a few hours) if a temperature gradient (TG-CVI), a pressure gradient (PG-CVI) or a combination of both (F-CVI, with F for forced) are applied to the preform [14, 15]. One way is to accelerate deposition in the core (raising its temperature) keeping the preform external surface at a low temperature to avoid pore entrance sealing while injecting the gaseous reactant under pressure in the preform through this relatively cold surface. All these modified-CVI processes suppose some fixturing applied to the preform to generate the gradients, at the expense of flexibility. Finally, in the related calefaction (or film boiling) process, the fiber preform is directly immersed in a boiling liquid precursor, the reactant being vaporized in the preform porosity. Here, the core is set at high temperature while the preform external surface is maintained at low temperature, i.e. the boiling point of the precursor. The high deposition rate and short densification time result again from the steep inward temperature gradient and the fact that the process is run at the atmospheric pressure [16, 17]. Although these variants of the CVI-process seem attractive, they have not been transferred yet, as far as we know, to the plant level, I-CVI remaining the process of choice at this level. Finally, CVI did not have the same success for oxide-matrix composites, although its feasibility for alumina, zirconia and  $Y_2O_3$ -stabilized zirconia has been established a long time ago, at least at the laboratory level [11, 12].

### Liquid phase route

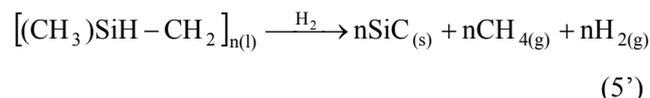
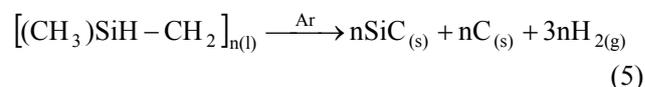
In the liquid phase route, the matrix is formed from a liquid precursor, in the fiber architecture. The precursor is first infiltrated in the reinforcement, then the solvent (if there is any) is evaporated and the residue is calcined/decomposed and finally sintered at moderate temperatures. The precursor can be an element in the molten state (Al for alumina or Si for SiC), a polymer, a sol or a slurry. There are many variants in the liquid phase route [18].

### Polymer infiltration and pyrolysis (PIP)

In the PIP-process, the matrix precursor is a polymer used in the molten state or in solution, such as a polycarbosilane (PCS) for Si-C, a polysilazane (PSZ) for Si-N, a polycarbosilazane (PCSZ) for Si-C-N or a polyborocarbosilazane (PBCSZ) for Si-B-C-N ceramics, respectively. Typically, the process involves four steps: (i) the infiltration of the liquid precursor in the preform,

e.g. by a technique similar to the resin transfer moulding (RTM), a pressure being applied to the liquid and the preform set in the mould which is maintained under vacuum, (ii) the *in situ* curing of the polymer, (iii) the pyrolysis of the polymer at about 1000°C and (iv) the sintering of the mineral residue [19-21].

One of the advantages of the PIP-process is that it relies upon well-known technologies. Further the pyrolysis residue is amorphous or nanocrystalline and can be sintered at relatively low temperatures. Finally, the process is well suited to matrix of complex composition, e.g. from the Si-B-C-N system. Conversely, the PIP-process displays several drawbacks. Firstly, gaseous species are formed during the pyrolysis step lowering the ceramic yield and resulting in a porous pyrolytic residue according to the following overall equations, written schematically for a Yajima's type PCS precursor [22]:

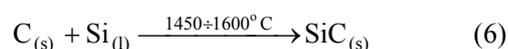


and corresponding to a ceramic yield of  $\approx 90$  and 69%, respectively. Hence, several PI-P sequences (typically, from 6 to 10) are necessary to achieve a high enough densification. The yield of pyrolysis can be improved by loading the liquid precursor with a powder, but this addition increases the precursor viscosity rendering more difficult the infiltration step. Hence, designing low cost polymer precursors with a high ceramic yield and which could be cured easily, remains a challenge [23, 24]. Secondly, composites fabricated by PIP also exhibit a noticeable residual porosity.

### Reactive melt infiltration (RMI)

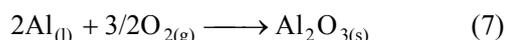
In the RMI-process, a fiber preform is infiltrated with an element in the molten state, the latter reacting with the preform or with the atmosphere, to form the ceramic matrix *in situ*. The process is well suited to elements with relatively low melting points, such as aluminum for the growth of alumina matrix or silicon for that of SiC-matrix.

When applied to SiC-matrix composites, the RMI-process involves two main steps. Firstly, a preform (the fibers being coated with an appropriate interphase) is consolidated with a reactive carbon, resulting from the pyrolysis of a liquid organic precursor. In a second step, it is infiltrated with liquid silicon at a high enough temperature, which reacts with the carbon to form SiC (Fig. 1b):



Carbon if wetted by liquid silicon climbing in the preform under the effect of capillary forces. When the amount of carbon deposited in the first step and the liquid silicon flow have been properly adjusted, the preform porosity can be almost totally filled with the *in-situ* formed ceramic matrix [25, 26]. RMI is a fast process which yields near net shape composites with very low residual porosity ( $V_p < 5\%$ ) and hence high thermal conductivity and hermeticity. Conversely, it is a high temperature process requiring the use of fibers with a high thermal stability, such as HM-carbon fibers or stoichiometric SiC fibers. Further, liquid silicon being very reactive, the interphase should be protected. One possibility is to use a dual interphase, such as PyC--SiC or BN-SiC fiber coating. Finally, the SiC-based matrix often contains significant amounts of free silicon. One way to solve this problem is to replace silicon by a suitable alloy (such as a Si-Mo alloy), Mo reacting with excess silicon to form the refractory MoSi<sub>2</sub> silicide.

RMI can also be used to form an alumina matrix in the pore network of a preform, the low melting point of aluminum greatly facilitating the infiltration. Here, the liquid precursor (an Al-based alloy) climbs in the preform where it reacts with the atmosphere that contains oxygen, to form *in-situ* an alumina matrix [27, 28]:



Composites fabricated by this process (an example being the DIMOX-process, initially developed by Lanxide, USA) display most of the advantages and drawbacks previously discussed for their SiC-matrix counterparts. The interphase (and even the fibers when they are non-oxide) should be protected. Further, the alumina-based matrix also contains significant residual metal alloy which should be eliminated if the composite is to be used at high temperatures.

### Ceramic (or powder) route

CMCs can also be fabricated following a route, referred to as the ceramic route, commonly used for monolithic ceramics. In its principle, this route comprises the following steps: (i) the impregnation of the reinforcement with a suspension of particles in a liquid, such as a sol or a slurry, often containing a fugitive binder and sintering additives, (ii) the evaporation of the solvent, (iii) a calcination at moderate temperature to remove the binder and decompose the organic additives, (iv) a sintering step at high temperature and usually under pressure. This is a generic process, initially applied to glass-ceramic matrix composites [27] and further extended to many oxide or non-oxide composites.

In its initial version, the slurry impregnation and hot-pressing (SIHP) process has been used to fabricate glass-ceramic matrix composites with carbon or SiC-based fibers [27-29]. A fiber tow is first impregnated

with a slurry containing a binder and wound on a mandrel, yielding an impregnated (green) 1D-ply similar to the prepreg commonly used in polymer matrix composite technology. Then, the plies are stacked according to a given sequence of fiber orientations. The plies assembly is dried and the binder vaporized (or burnt out). It is set in the die of a press and sintered under pressure at a high enough temperature. Finally, the composite is annealed (ceramization step) in order to partially crystallize the matrix. The SIHP-process displays two important advantages: (i) it relies on well-known technologies and (ii) it yields composites with low residual porosity, a feature which results, for these matrix compositions, from the intermediate formation of a glass (flowing in the liquid state between the fibers under pressure) further converted into a partially crystallized ceramic matrix. The SIHP-process has been extended to non-oxide covalent matrices, namely SiC and Si<sub>3</sub>N<sub>4</sub> [30-34]. The main difficulties here result from the well-known poor sintering ability of SiC and Si<sub>3</sub>N<sub>4</sub> powders and correlatively the risk of fiber degradation. To solve this problem, different approaches are used. Firstly, only fibers displaying a high thermal stability are employed, namely HM-carbon fibers or more recently stoichiometric SiC fibers (Tyranno SA fibers, from Ube Industries, for example). Secondly, very reactive matrix powders are selected. This includes nanosize powders ( $\beta$ -SiC, for example), as well as powders resulting from the pyrolysis (in step (iii)) of an organosilicon polymer added to the slurry. Thirdly, specific sintering additives usually forming a liquid phase at grain boundaries during sintering, are systematically used to lower the sintering temperature and to reduce the residual porosity. Examples of these additives are from the Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub> system for both Si<sub>3</sub>N<sub>4</sub> and SiC [30-34]. By combining these approaches, SiC- and Si<sub>3</sub>N<sub>4</sub>-matrix composites, with a residual porosity less than 5% and almost no fiber degradation, can be fabricated at 1720÷1820°C and 1450÷1600°C, respectively under a pressure of 5÷25 MPa. The so-called NITE-process (for nanoinfiltration and transient eutectics), relying on nanosize  $\beta$ -SiC powder and Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub> sintering additives, is a recent and convincing example of the application of the generic SIHP-process to non-oxide covalent ceramic matrices (Fig. 1c) [33, 34].

### Combined (or hybrid) routes

Since each of the routes depicted previously has its own advantages and drawbacks, it might well be appropriate to combine two (or more) of them in order to shorten the overall densification time or/and to lower the residual porosity or to design a matrix with a specific microstructure. There is a variety of such combined (or hybrid) processing routes.

Generally speaking, CVI is the method of choice for the deposition of the interphase, on the fibers of a preform, whatever the method further used to infiltrate the matrix. Both CVI and PIP yield composites with a significant residual porosity. Although this porosity can be sealed with an overcoating by CVD/CVI, such a coating often undergoes microcracking. Hence, it could be more appropriate to add one RMI-step, liquid silicon (or any other suitable liquid alloys) filling the residual porosity and rendering hermetic the composite. Still more complex processing patterns have been envisaged [35]. Interestingly, combined processing routes can also be used to design matrices with a specific microstructure, e.g. a porous matrix strongly bonded to the fibers, i.e. without a weak interphase [36, 37]. Here, the processing comprises a pressure infiltration of the preform with a slurry followed by several PIP steps to strengthen the matrix (but at a pyrolysis temperature low enough to avoid its full sintering).

## MATERIALS DESIGN

### Selection of constituents

#### Reinforcement

The best reinforcement for CMCs would be *carbon fibers* on the basis of their mechanical and thermal properties at high temperature, density and cost. Further, since they have a small diameter, they also display a good weaving ability and can be used to produce nD-preforms of complex shapes. Unfortunately, they are oxidation prone, their oxidation rate becoming noticeable at 500°C. SiC fibers are an alternative to carbon fibers. SiC is a light and refractory material and one of the most creep-resistant ceramics. Further, it displays a relatively high thermal conductivity. Finally, it has a well known oxidation resistance up to 1500°C as long as a dense and adherent silica scale is formed (passive oxidation). SiC-based fibers have been available for a long time [22, 38]. However, the first fibers (Nicalon fibers, from Nippon Carbon, Japan) were Si-C-O fibers, produced from a PCS-precursor cured with oxygen, and consisting of SiC-nanocrystals and free carbon in an amorphous  $\text{SiC}_x\text{O}_y$  phase. They were weavable since their stiffness is relatively low ( $E \approx 200$  GPa) due to their composition. Unfortunately, these fibers undergo decomposition at 1100–1200°C with strength degradation. More recently, oxygen-free SiC + C fibers (Hi-Nicalon, also from Nippon Carbon) or SiC-fibers (Hi-Nicalon type S, from Nippon Carbon, Tyranno SA, from Ube Industries, Japan or Sylramic from Dow Corning, USA) became available, with much better thermal stability, thermal conductivity and mechanical properties at high temperatures (the best being stable up to almost 2000°C and creep resistant up to  $\approx 1500^\circ\text{C}$ ) (Fig. 2) [39–

41]. However, their stiffness and large diameter make their weaving problematic. Further, their strain at failure is low, which considerably reduces the domain of non-linear behavior, in the related composites. Finally, their present cost is dissuasive. Obviously, the best reinforcement for CMCs exposed to oxidizing atmospheres should be oxide fibers. There is a number of refractory oxides which have been produced as small diameter fibers such as mullite, alumina or stabilized zirconia, some of them being relatively light and stiff. However, most oxide fibers suffer from two weak points: (i) grain growth at medium temperature with strength degradation and (ii) poor creep resistance beyond  $\approx 1000^\circ\text{C}$  [42, 43]. The most promising candidates are mullite and YAG, pure or mixed with a secondary phase. The best of them, consisting of a mixture of mullite and corundum (Nextel 720, from 3M, USA), has a maximum use temperature of about 1200°C [44]. Further, oxide fibers exhibit low thermal conductivity, high coefficient of thermal expansion and poor thermal shock resistance.

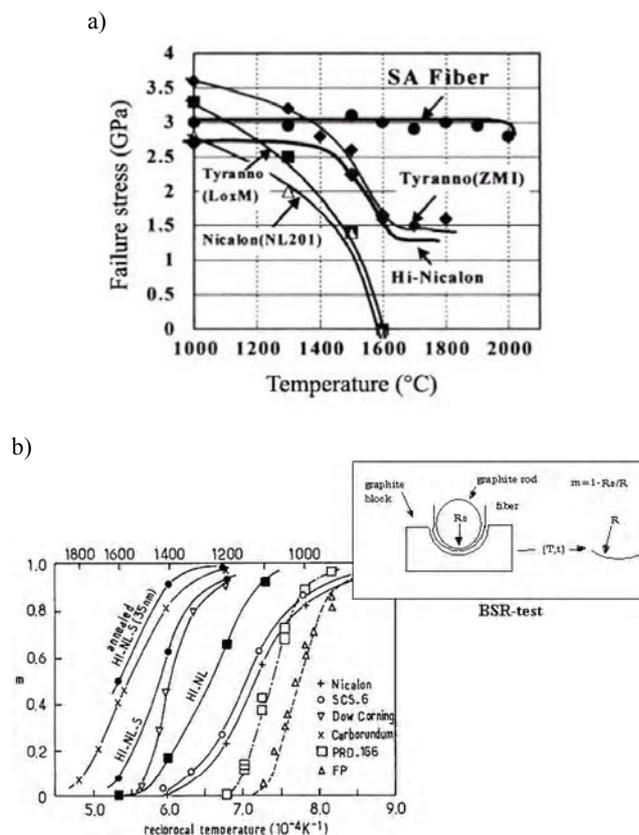


Fig. 2. Effect of an annealing treatment on the mechanical behavior of ceramic fibers: a) variations of the room temperature ultimate failure stress of different SiC-based fibers as a function of the annealing temperature (according to T. Ishikawa et al. [40]), b) variations of the relaxation parameter  $m$  of the BSR-test as a function of the annealing temperature for different ceramic fibers (according to M. Takeda et al. [115])

Rys. 2. Wpływ starzenia na własności mechaniczne włókien ceramicznych: a) zmiany naprężenia niszczonego w temperaturze pokojowej dla różnych włókien na bazie SiC w zależności od temperatury starzenia, wg T. Ishikawa i in. [40], b) zmiany parametru relaksacji  $m$  w teście odprężania przy zginaniu (BSM) w zależności od

temperatury starzenia dla różnych włókien ceramicznych, wg M. Takeda i in. [115]

## Matrix

There are two families of matrices: non-oxides and oxides. Although this is not a general rule, the nature of the matrix and that of the reinforcement are often chosen close to one another in order to avoid chemical and thermo-mechanical compatibility problems. This is typically the case for C/C and SiC/SiC composites whereas C/SiC composites display a microcracked SiC-matrix due to CTE-mismatch, and SiC/glass-ceramic composites raise FM-reaction issues.

Carbon is the matrix of choice in application where the composites have to withstand extremely high temperatures and ablation for short periods of time. It is also selected when specific properties are required, such as friction or bio-compatibility. Further, the carbon matrix can be formed with a variety of structure and microtexture and consequently a variety of properties, on a cost-effective basis. Silicon carbide is preferred in composites exposed for long periods of time to oxidizing atmospheres or/and when hardness is required (wear resistance). Further, it has a relatively high thermal conductivity, when dense and crystalline. However, its oxidation becomes active and it is attacked by hydrogen and steam, at high temperatures. Conversely, silicon nitride, which is one of the major monolithic structural ceramics, has not been extensively used as matrix in CMCs.

In the oxide-matrix family, SiO<sub>2</sub>-based glass-ceramics, which have been the very first ceramic matrix ever used [45, 46], still have a high potential [27-29]. Composites with this kind of matrix have, in some way, common features with their polymer-matrix counterparts: (i) the matrix is more compliant than the reinforcement, (ii) it can be readily deformed in its state of low viscosity, yielding composites with almost no residual porosity when processed by SIHP. The matrix can be further crystallized and stiffened by annealing. The matrix composition and properties can also be widely varied, with maximum use temperature increasing from 600°C to about 1250°C. Their coefficient of thermal expansion (CTE) are close to that of SiC-based fibers and can be adjusted by changing the composition. Finally, SiO<sub>2</sub>-based glass-ceramic matrix composites actually raise FM chemical reaction problems, which can be regarded either as a drawback or an advantage depending on the respective composition of the constituents. As an example, an *in-situ* formed weak interphase acting as a mechanical fuse, results from FM reaction in SiC fiber/LAS composites. Other oxide matrices can be used in CMCs, such as alumina-based matrices when more refractoriness is needed. Finally, ultra-refractory oxide matrices, such as stabilized zirconia, can also be used

for their thermal stability, chemical inertia or electrical ionic conductivity.

## Selection of a concept of damage tolerance

CMCs comprise intrinsically brittle constituents. Further, they are inverse composites (the failure strain of the matrix  $\varepsilon_m^R$  is lower than that of the fibers  $\varepsilon_f^R$ ) at variance to most polymer (or metal) matrix composites. Consequently, it is the matrix which fails first under loading [1]. Depending on how the composite has been designed and fabricated, the microcracking of the ceramic matrix may or may not lead to the early failure of the fibers by notch effect. The most classical way to avoid the early fiber failure is through the addition of a mechanical fuse (to protect the fiber) at the fiber surface, the interphase, to weaken the FM-bonding, arresting or deflecting the matrix microcracks [4-6]. More recently, a new concept of damage tolerance, relying on the use of a porous matrix and strong FM-bonding, has been proposed [36, 37].

### The „weak” interphase concept

In a CMC, the FM-bonding should not be too strong (otherwise, the composite behaves in a brittle manner) nor too weak (in such a case, the FM load transfer would be poor). Hence, the FM-bonding should be carefully controlled. In the „weak” interphase concept, a thin layer of a compliant material with a low shear stress, is formed at the fiber surface. The matrix microcracks are arrested or/and deflected in the interfacial zone if its failure energy  $\Gamma_i$  is lower than that of the fiber  $\Gamma_f$  (with typically,  $\Gamma_i/\Gamma_f \leq 1/4$ ) [47-50]. There are several ways to introduce a weak link in the FM-interfacial zone, the most classical being: (i) a film forming a weak bond with either the fiber or the matrix (the monazite interphase in alumina-based all-oxide composites), (ii) a film with a layered crystal structure or microstructure (pyrocarbon interphase in non-oxide CMCs) or (iii) a layer of porous material (a layer of porous SiC in SiC/SiC composites) (Fig. 3) [5, 6, 50, 51]. The interphase has typically a thickness of a few 100 nm or less. Its function is complex, including: matrix microcrack deflection, FM-load transfer, diffusion barrier and thermal residual stress relaxation. Further, it should be compatible with both the fiber and the matrix, as well as with the environment.

An interphase can be formed *in-situ* during the high temperature step of processing, as the result of FM-interactions, or deposited (by CVD/CVI) on the fiber surface prior to the infiltration of the matrix. As an example of reaction formed interphases, the first interphases used in SiC/LAS composites were formed *in-situ* during the hot pressing step of the SIHP-process, and reported to consist of a layer of carbon with NbC

nanocrystals. Carbon was thought to result from the decomposition of the Si-C-O (Nicalon) fiber, whereas NbC was formed by reaction between carbon and Nb<sub>2</sub>O<sub>5</sub> added to the LAS-composition as a secondary phase [52, 53]. The main problem lies in the control of their growth formation, which depends on many parameters. Hence, the general tendency is to prefer interphases deposited (e.g. by CVD/CVI) on the fibers prior to the infiltration of the matrix.

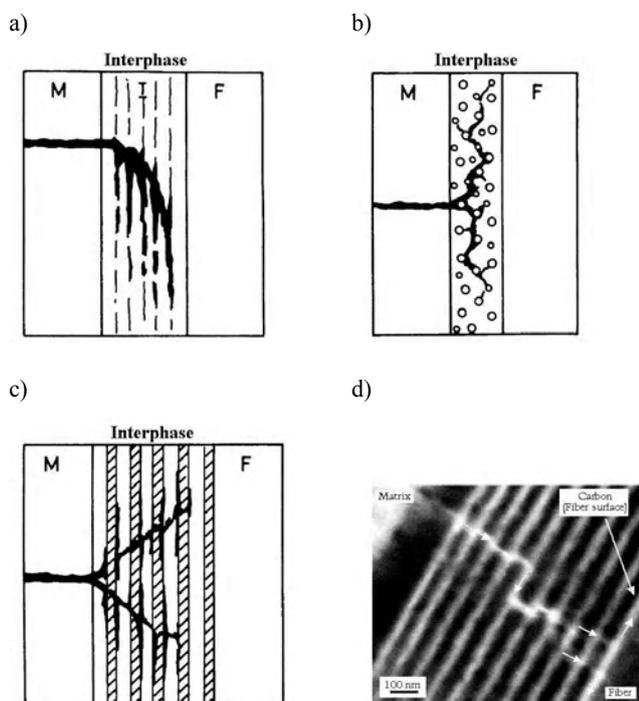


Fig. 3. Different interphase concepts: a) single pyrocarbon or BN layer interphase, b) porous SiC single layer, c) multilayered (X-Y)<sub>n</sub> interphase with X = PyC or BN and Y = SiC, d) crack deflection in a (PyC-SiC)<sub>10</sub> interphase, according to R. Naslain (a, b, c) [5] and Bertrand et al. ref. [58]

Rys. 3. Różne modele fazy przejściowej: a) faza przejściowa z pojedynczej warstwy węgla pirolitycznego (PyC) albo BN, b) pojedyncza warstwa porowatego SiC, c) wielowarstwowa faza przejściowa (X-Y)<sub>n</sub>, gdzie X oznacza węgiel pirolityczny albo BN, zaś Y oznacza SiC, d) odchylenie pęknięcia w fazie przejściowej (PyC-SiC)<sub>10</sub>, R. Naslain (a, b, c) [5] i S. Bertrand i in. [58]

It has been postulated that the best interphase materials might be those with a layered crystal structure or microstructure, the layers being parallel to the fiber surface, weakly bonded to one another but strongly bonded to the fiber. This last condition is important. If it is not satisfied, crack deflection rather occurs at the surface of the fibers which becomes exposed to the atmosphere. The number of materials with a layered crystal structure is limited. These are: pyrocarbon and boron nitride, for non-oxide composites and mica-derived oxides and magnetoplumbite-type phases (such as hibonite CaAl<sub>12</sub>O<sub>19</sub>) for oxide composites [5, 6, 51]. Hence, the concept has been extended to multilayered interphases. Dual interphases, such as BN/SiC, are commonly used in reactive systems (SiC/oxide composites) or reactive

processing (RMI or DIMOX), in which the BN layer in contact with the fiber acts as mechanical fuse whereas the SiC layer protects both of them from reaction with the matrix or the environment [54, 55]. Further, (PyC-SiC)<sub>n</sub> or (BN-SiC)<sub>n</sub> (with typically, 4 < n < 10) have been suggested for SiC/SiC composites to reduce the oxidation of the PyC or BN mechanical fuses. In these highly engineered interphases, the thickness of the PyC or BN layers is reduced to a few 10 nm, the B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub> fluid oxide phases formed by oxidation, healing the narrow annular pore which is created around each fiber by oxidation and slowing down the oxidation process. Such multilayered interphases can be conveniently deposited by P-CVI, according to the overall equations (1) to (3) [5, 56-59].

### The porous matrix concept

Flaw tolerant CMCs can also be designed through the use of a *porous* matrix based on the fact that a crack can propagate in such a matrix without exerting a notch-effect on the brittle fibers at variance to what happens in a dense matrix [36, 37]. As a consequence, a weak interphase is no longer needed and the bond between the fibers and the matrix can be “strong”. In such composites, cracks formed in the fiber bundles (mode I) can be deflected in the porous matrix parallel to the fiber direction if: (i) the fiber bundles are heterogeneous, (ii) the porous matrix has a low mode II (shear) fracture energy,  $\Gamma_m^{II}$ , relative to the mode I (opening) fracture energy of the fiber bundle,  $\Gamma_b^I$  (with  $\Gamma_m^{II} / \Gamma_b^I \leq 0.5$ ) and (iii) the matrix is in a state of residual compression stress, i.e. the CTE of the matrix is lower than that of the fiber [36]. Such is the case for mullite or silicon nitride matrices reinforced with polycrystalline alumina-based fibers [37]. Although the use of porous matrices provides an interesting concept for designing flaw-tolerant CMCs, it exposes the fibers to the atmosphere. Consequently, this concept can be applied only to oxidation-resistant fibers.

## PROPERTIES

### Mechanical behavior

CMCs comprising a continuous fiber reinforcement display a non-brittle behavior when the FM-bonding has been properly optimized e.g. through the use of a „weak” interphase [1, 4, 8, 47-49].

Under monotonous tensile loading, CMC stress-strain curves exhibit first a linear elastic domain, which is followed by a domain of *non-linearity* corresponding to the development of different damaging phenomena and resulting in stiffness decrease [60]. Hence, they display an elastic damageable behavior. Firstly, the brittle matrix undergoes multiple microcracking, the micro-

cracks propagating, for 1D-composites loaded in the fiber direction, in planes perpendicular to the fiber direction (mode I). The microcrack density, i.e. the number of crack per unity of length in the fiber directions, is directly related to the FM-bonding: it is low for weak FM-bonding and it increases as that bonding becomes stronger. Secondly, the matrix microcracks being deflected in the FM-interfacial region (mode II), the fibers are debonded over a certain length,  $l_d$ , which is also related to the FM-bonding,  $l_d$  being long for weak bonding and short for strong bonding. The fibers are said to bridge these transverse microcracks. As strain increases, the opening of the matrix microcracks increases. At a given strain value, it remains small if the microcrack density is high but it can be relatively large when only few microcracks are formed. Unloading-reloading cycles are often applied in the non-linear domain. They usually show an hysteresis, related to friction phenomena at the debonded FM-interface and occurrence of residual stress, and whose features can be used to characterize the residual Young's modulus and FM-bonding [61]. Ultimate failure occurs with fiber pull-out. The mean length,  $l_p$ , of the pulled-out fibers also depends on FM-bonding: it is large when this bonding is weak, but short (a few 10  $\mu\text{m}$ ) for relatively strong bonding.

The shape of the stress-strain tensile curve also depends upon the design of the FM-interfacial zone. It often exhibits a plateau (or a plateau-like feature) at the end of the linear elastic domain, observed for composites with a low FM-bonding [1]. At the end of this plateau, the fibers are debonded almost all over their entire length and the load mainly carried by the fibers. Conversely, when the FM-bonding is stronger, and particularly the fibers strongly bonded to the interphase, such a plateau is not observed, matrix microcracking continuing under raising stress almost up to ultimate failure (Fig. 4). Under such conditions, some load transfer remains effective up to failure (which occurs at a higher stress), crack density is high and both crack opening and debond length are small [56]. Finally the stress-strain tensile curves of composites with a porous matrix is quasi-linear up to failure, although microcracking actually occurs in the matrix, the porous matrix being almost reduced to powder when the fibers fail. This behavior reflects the major role played by the strong fibers (and the modest contribution of the matrix) [37, 62]. All the damaging phenomena depicted above absorb significant amounts of energy, with the result that the fracture energy can be extremely high, e.g. several  $\text{kJ/m}^2$  for 2D-C/SiC and 2D-SiC/SiC composites, compared to that for the related monolithic ceramics (a few  $100 \text{ J/m}^2$  only, for sintered SiC) [7].

The tensile behavior of most CMCs does not change markedly up to about  $1000\div 1100^\circ\text{C}$ . However, some change may occur due to the thermal evolution of the

constituents or/and the relaxation of the thermal residual stresses. As an example, the mechanical behavior of SiC (Nicalon)/BN-SiC/BMAS composites remains non-linear when temperature is raised from 25 to  $1200^\circ\text{C}$  in air and failure still occurs with fiber pull-out, on the one hand, but the UTS and strain at failure increase whereas both the proportional limit and Young's modulus decrease, on the other hand [63]. As expected, the high temperature mechanical behavior of composites with a porous matrix is mainly controlled by the fibers [64].

Fig. 4. Tensile curve of a 2D-SiC (Nicalon)/PyC/SiC (CVI) composites with a strong fiber/interphase bonding showing the non-linear stress-strain behavior, hysteresis unloading-reloading cycles, permanent strain upon unloading ( $\epsilon_T^R$ ) and acoustic emission (A.E.C.). The insert shows the matrix crack deflexion in the interphase, according to C. Droillard, ref. [116]

Rys. 4. Krzywa rozciągania dla kompozytów 2D-SiC (Nicalon)/PyC/SiC otrzymanych metodą CVI o silnym wiązaniu włókien z fazą przejściową, pokazująca nieliniową zależność naprężeniowo-odkształceniową, pętle histerezy podczas cyklicznego obciążania i odciążania, trwale odkształcenie przy odciążeniu ( $\epsilon_T^R$ ) i emisję akustyczną (A.E.C.). Wstawka pokazuje odchylenie pęknięcia osnowy w fazie przejściowej, wg C. Droillard [116]

The mechanical behavior of CMCs is also time-dependent. Most of them exhibit a progressive reduction of strength and Young's modulus, as well as an increase in permanent strain upon unloading, with cycling. There is a threshold stress below which fatigue failure does not occur. This threshold value, relative to the pristine ultimate tensile stress is much higher than that reported for metals. Further, if the maximum applied stress is higher than the stress at which the first crack appears in the matrix, multiple cracking of the matrix occurs, mainly during the first cycle. During further cycling, there is a wear of the fibers, the matrix and the interphase. Finally, frequency has a limited influence on the fatigue behavior as long as it remains low (0.3 to 10 Hz). Conversely, it drastically affects fatigue life when it is high (10 to 400 Hz), this change being attributed to frictional heating along the FM-interfaces [64-66].

CMCs creep when loaded at high temperature but their creep rate remains actually low under conditions

where most metals and superalloys can no longer be utilized. As an example, the creep rate of both 1D-Nicalon/BN-SiC/BMAS (0/90°) and 2D-Nicalon/PyC/SiC (CVI) composites are of the order of  $2 \cdot 10^{-9} \text{ s}^{-1}$  at 1100°C under an applied stress of 100 MPa. For the latter, it is still low and of the order of  $4 \cdot 10^{-8} \text{ s}^{-1}$  at 1400°C [63, 67]. The creep of CMCs depends upon many parameters. CMC creep curves may display the three classical creep stages (transient, stationary and accelerated) or only one or two of them [63, 67-69]. Creep in CMCs occurs according to different mechanisms depending on the creep mismatch ratio (CMR) defined as the ratio between the creep rate of the fiber  $\dot{\epsilon}_f$  and that of the matrix  $\dot{\epsilon}_m$  ( $\text{CMR} = \dot{\epsilon}_f / \dot{\epsilon}_m$ ) [67, 69]. When  $\text{CMR} < 1$  (glass-ceramic matrix composites), there is a time dependent transfer of load from matrix to fibers which can lead to fiber failure and fragmentation. Conversely when  $\text{CMR} > 1$  (composites with  $\text{Si}_3\text{N}_4$  or SiC covalent matrix), load is transferred from fibers to matrix promoting matrix microcracking. As a result, changing the composition of the fibers (moving, for example, from Si-C-O Nicalon fibers containing a glassy phase to quasi-stoichiometric oxygen-free SiC fibers) or/and of the matrix may change the load transfer and creep mechanism. Generally speaking, CMC creep should be discussed in terms of damage accumulation (the so-called damage-creep mechanism) rather than on the basis of conventional approaches used for metals or monolithic ceramics [67, 70].

### Thermal behavior

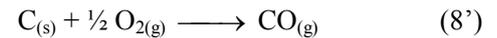
Thermal conductivity is one of the key parameters which control the thermal shock resistance of materials, that of CMCs depending upon both the nature of the constituents and microstructure [71, 72]. Oxide fibers and matrices display low thermal conductivities with the result that most oxide-oxide composites are insulating materials. The same is true for composites fabricated with  $\text{Si}_3\text{N}_4$ -based fibers or matrices. Conversely, carbon fibers and pyrocarbon matrix exhibit high thermal conductivities when fabricated from so-called graphitizing carbons and further heat treated at very high temperatures (typically,  $\text{HTT} > 2500^\circ\text{C}$ ). However, the thermal conductivity of those graphitic carbons is strongly anisotropic: it is high parallel to the graphene layers ( $K_{//}$ ) and low in a perpendicular direction ( $K_{\perp}$ ) ( $K_{//}/K_{\perp} \approx 400$  for graphite). By contrast, poorly organized or amorphous carbons have a low thermal conductivity. Hence, C/C composites exhibit either a high thermal conductivity (with  $K_{//} = 80\div 150 \text{ Wm}^{-1}\text{K}^{-1}$  and  $K_{\perp} = 5\div 20 \text{ Wm}^{-1}\text{K}^{-1}$  for 1D-composites at 25°C), a property used in C/C brakes, or a low conductivity, as in rocket nozzles, depending on their processing conditions [73]. Finally, SiC also displays a high thermal

conductivity ( $K = 60\div 70 \text{ Wm}^{-1}\text{K}^{-1}$  for both quasi-stoichiometric SiC fibers (Tyranno SA, for example) and dense SiC(CVI) matrix, at room temperature but which progressively decreases as temperature is raised  $\approx 30 \text{ Wm}^{-1}\text{K}^{-1}$  at  $\approx 800^\circ\text{C}$ ) [74]. The thermal conductivity of carbon or SiC-based composites also depends upon microstructural considerations. As an example, the occurrence of secondary phases as well as residual matrix porosity after processing, considerably reduces the thermal conductivity. Consequently, SiC/SiC composites fabricated from quasi-stoichiometric fibers by RMI, SIHP ( $V_p < 5\%$ ) have a higher conductivity than composites produced by PIP or CVI ( $V_p = 10\div 15\%$ ) [33, 75]. The coefficient of thermal expansion usually obeys rules of mixture [71]. It is high when both composite constituents have high CTE (such as in alumina/alumina composites) and low (and even nil) in the reverse situation. This is typically the case for SiC-matrix reinforced with HM or UHM-carbon fibers known to have negative CTE.

### Effect of the environment

#### Oxidation chemistry

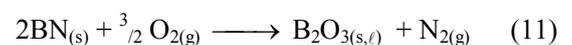
Non-oxide CMCs, such as C/C, C/SiC and SiC/SiC composites are intrinsically oxidation-prone [9, 10]. The oxidation regime is active when it occurs with formation of gaseous species exclusively. This is typically the case for the oxidation of carbon fibers, PyC interphase and carbon matrices, which starts at temperature as low as  $\approx 450^\circ\text{C}$  (Fig. 5):



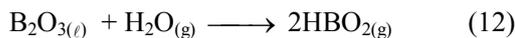
but also for that of SiC itself, at high temperatures and under low oxygen partial pressure [76]:



Active oxidation of CMCs is an in-depth phenomenon, which can destroy rapidly the materials since it consumes the reinforcement, the PyC-interphase and even the matrix itself. Conversely, in the passive oxidation regime, a condensed oxide, such as  $\text{SiO}_2$  or  $\text{B}_2\text{O}_3$ , is formed usually with an increase in molar volume (Fig. 5) [77]



The oxide scale is usually covering (the  $\Delta$  - parameter, defined as the ratio between the molar volumes of the oxide which is formed and the non-oxide which is consumed, being larger than 1) and adherent, with the result that oxygen has to diffuse across that scale to further react with the substrate. Since this diffusion is slow, the in-depth oxidation is considerably slowed down. The oxide scale is often amorphous (silica) or even liquid (boria) and it has a healing effect, i.e. it can seal the microcracks of the composite. Finally, water vapor can modify drastically the oxidation process, promoting the volatilization of the protective scale ( $B_2O_3$ ;  $SiO_2$  or  $SiO_2$ - $B_2O_3$ ), tentatively according to [78-80]:



Hence, CMCs should be designed in a way to protect the oxidation-prone constituents against oxidation by applying a coating to the composite or/and by a proper design of the material.

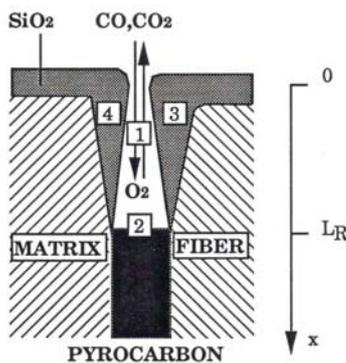


Fig. 5. Phenomena occurring during the oxidation of a 1D-SiC/PyC/SiC model composites: 1 - diffusion of oxygen and carbon oxides along annular pore formed by oxidation around each fiber, 2 - gasification of the PyC-interphase at the bottom of the pore, 3 - and 4 - silica scale formed on pore walls in the passive oxidation regime, according to ref. [77, 117]

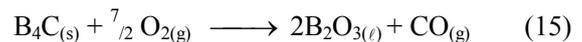
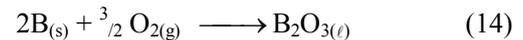
Rys. 5. Zjawiska występujące podczas utleniania kompozytu 1D-SiC/PyC/SiC: 1 - dyfuzja tlenu i tlenków węgla wzdłuż pierścieniowego poru tworzącego się wskutek utleniania wokół każdego włókna, 2 - zgazowanie fazy przejściowej PyC na dnie poru, 3 i 4 - zgorzelina krzemionkowa utworzona na ściankach poru w warunkach pasywnego utleniania [77, 117]

### Protective coatings

The design of an efficient coating to protect non-oxide CMCs against oxidation is not straightforward since the constraints are multiple, including: low oxygen permeability, erosion and corrosion resistance as well as chemical and thermomechanical compatibility with the substrate, under temperature/load cycling. The best design solution is through a multilayered coating comprising a bond layer, one or several functional active layers and an outer (or primary) erosion-resistant/oxygen bar-

rier layer, the overall coating displaying a self-healing capability [73].

For the protection of C/C or C/SiC composites, the bond layer is often SiC and the outer layer either SiC or  $Si_3N_4$  (both being hard and forming an adherent silica scale with a low oxygen permeability). The functional active layer located in between usually comprises phases, such as boron,  $B_4C$  or  $SiB_6$ , or mixtures from the Si-B-C ternary system, which form fluid oxides when exposed to oxidizing atmospheres [81]:



$SiB_{6(s)} + \frac{11}{2} O_{2(g)} \longrightarrow SiO_{2(s,l)} + 3B_2O_{3(l)} \quad (16)$   
and heal the cracks of the coating within a wide temperature range. By optimizing both the chemical composition of the layers and their thicknesses, such multilayered coatings provide efficient protection to C/C and C/SiC composites up to  $\approx 1500^\circ C$  in air [81].

The coating design constraints are still more severe for non-oxide CMCs exposed to wet oxidizing atmospheres under high pressure, which is typically the case for SiC/SiC composites in aerojet engines or cogeneration gas turbines since, under such conditions, there is a volatilization of the protective silica scale (see equation (13)) and a corrosion of SiC (referred to as a recession). Hence, SiC should itself be protected with a suitable coating. A solution, could be again a multilayered EBC comprising: a silicon bond layer, (easy to form in the RMI-process), a mullite (or better, a mullite + BSAS mixture) as intermediate diffusion barrier layer and finally a BSAS top coat, where BSAS stands for a baryum strontium aluminosilicate. SiC/SiC composites with such EBC may have an upper temperature limit of  $1300 \div 1400^\circ C$  for over 10,000 h lifetime [82].

### Self-healing matrices

The concept of self-healing, based on the use of glass-formers in oxidizing atmospheres can be applied to the matrix, following two material design and processing approaches: (i) addition of glass-former filler to the matrix, in the PIP or SIHP processes or (ii) deposition of a suitable multilayered matrix by CVI. Adding a B-based filler (boron,  $B_4C$ ,  $SiB_6$ ) to the matrix liquid precursor in the PIP or SIHP processes, is relatively straightforward, for either C or SiC-matrix composites. In an oxidizing atmosphere, oxygen diffusing along cracks will react with the filler (equations (14) to (16)) to form a fluid oxide phase, healing the cracks and slowing down the in-depth oxygen diffusion and overall oxidation rate [83].

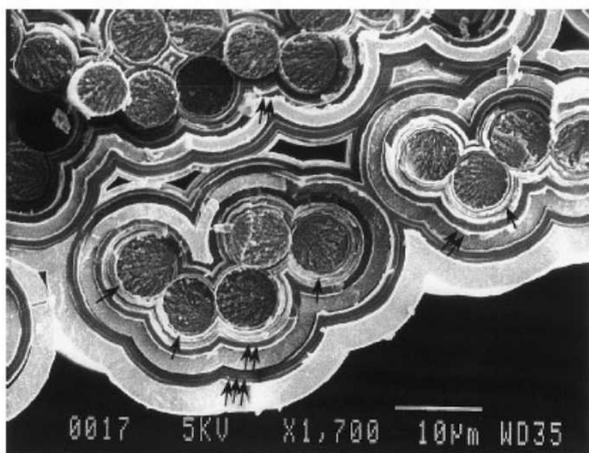


Fig. 6. Improvement of the oxidation resistance of non-oxide CMCs through the use of self-healing matrices, according to ref. [84]

Rys. 6. Podwyższenie odporności na utlenianie kompozytów o osnowie ceramicznej niezawierających tlenków przez zastosowanie osnów samoregenerujących [84]

Another design/processing approach to produce self-healing matrices in SiC-matrix composites is to replace such a matrix by a multilayered SiC-based matrix (Fig. 6). The matrix comprises layers of mechanical fuses deflecting cracks and rendering their paths complex and longer, as well as layers of materials (e.g. from the Si-B-C ternary system or related binary systems) forming fluid oxides with healing capability. Oxygen diffusing along matrix cracks, reacts with the glass-formers. It is entrapped in the matrix as fluid oxide filling the cracks and slowing down oxygen in-depth diffusion and overall oxidation rate [84-86].

### Other properties

Among the other CMC properties which are of interest for applications, are friction, activation under nuclear radiations and bio-compatibility. C/C composites display mainly two friction regimes. In the low friction regime, which is associated with an interaction between carbon and the environment, e.g. the chemisorption of water molecules, the friction coefficient ( $\mu = 0.05 \div 0.10$ ) and the wear rate are low. In the high friction regime, both the friction coefficient ( $\mu = 0.30 \div 0.40$ ) and wear rate are higher. A transition between the former and the latter is observed when the water molecules are desorbed, e.g. when temperature is raised [87]. In terms of friction, C/C composites display two weak points: their properties depend upon the environment and they are oxidation-prone. Attempts have been done to improve their friction properties by replacing part of the C-matrix by SiC. Although the data are still limited in this field, it seems that the friction coefficients of C/SiC or C/C-SiC (Si) composites are higher ( $\mu = 0.40 \div 0.70$ ) than those

of conventional C/C composites. Further, their wear rates seem to depend strongly on composition (SiC is a hard phase relative to graphitic carbon) and processing [89, 90].

Most structural materials undergo change in volume (shrinkage or swelling) or/and mechanical properties and more importantly acquire a certain level of radioactivity, when they are exposed to nuclear radiations. Non-oxide CMCs and particularly SiC/SiC composites appear to be promising materials in this field, on the basis of their refractoriness, dimensional stability, mechanical properties at high temperature and low activation, with however several restrictions. Firstly, they should be preferentially made of pure  $\beta$ -SiC, i.e. ideally of stoichiometric  $\beta$ -SiC fibers embedded in a  $\beta$ -SiC matrix. Secondly, the interphase should contain as little carbon and BN as possible. An answer could be in the use of  $(\text{PyC-SiC})_n$  multilayered interphases with very thin PyC sublayers or that of porous SiC interphases. Thirdly, the residual porosity should be as low as possible to display a high thermal conductivity as well as a high hermeticity (with respect to species formed by nuclear reaction or/and fluids used to extract heat generated by nuclear reactions) [91-97].

Finally, C-based CMCs are known to display an excellent bio-compatibility and are envisaged for bone or tooth prostheses in place of metal alloys or polymers. Their mechanical properties can be easily tailored to match those of bones or teeth. There is no rejection tendency, even after long implantation time (as an example, neo-bone tissues were observed to grow within the residual open porosity of C/C implant). Further, the bio-compatibility and lifetime of C/C implants are expected to be good enough not to require to be replaced during patient life [72, 98, 99].

## APPLICATIONS

### Aeronautics and space

It is in the field of aeronautics and space that CMC applications are the most effective. The first applications were and are still, the nozzle of rocket engines and the re-entry thermal protection of nuclear warheads and spacecraft. C/C are here the materials of choice for extremely high service temperatures (up to  $\approx 3000^\circ\text{C}$ ) and short exposures. They are still employed but with a SiC-based coating in reusable thermal protection (space shuttles) when temperature is in the range of  $1300 \div 1700^\circ\text{C}$ , atmosphere being oxidizing and accumulated service exposures a few hours [3, 100, 102]. It is anticipated that the hot structures of next generation spacecraft could better be fabricated with SiC-matrix composites, as suggested by preliminary studies performed for the European Hermes and Japanese Hope programs [100, 101, 103]. The next challenge in this field,

is the introduction of CMCs in aerojet engines in place of superalloys, with a view to increase the combustion temperature (and consequently, the engine efficiency), to decrease the weight,  $\text{NO}_x/\text{CO}$  emission and noise level, and simultaneously to reduce the cooling systems (Fig. 7). It is generally accepted that superalloys have reached their limit in this field (they are already working near their melting point, utilized (blades) as gas-cooled single crystals and their density is high, i.e. typically  $8 \text{ g/cm}^3$ ) and should be replaced by more refractory materials, such as the new CMCs. The challenge here is in the very severe service conditions as well as in terms of lifetime, typically from few 1,000 to 10,000 hours. SiC-matrix composites seem to be the best materials for temperature ranging from 1200 to 1500°C and their use, first in military aerojet engines and non-rotating parts, is in progress. Exhaust nozzle outer flaps, with a service temperature not exceeding  $600\div 700^\circ\text{C}$ , fabricated with C/SiC composites and exhibiting a density of about  $2 \text{ g/cm}^3$ , are already in volume production [83, 86, 101, 104-106]. Inner flaps with higher service temperatures ( $800\div 1000^\circ\text{C}$ ) fabricated with a self-healing matrix [86, 101, 104, 105] as well as combustor liners (SiC/SiC composites with suitable EBCs) [26, 107-109] are presently ground bench tested [107, 109].

### Power generation

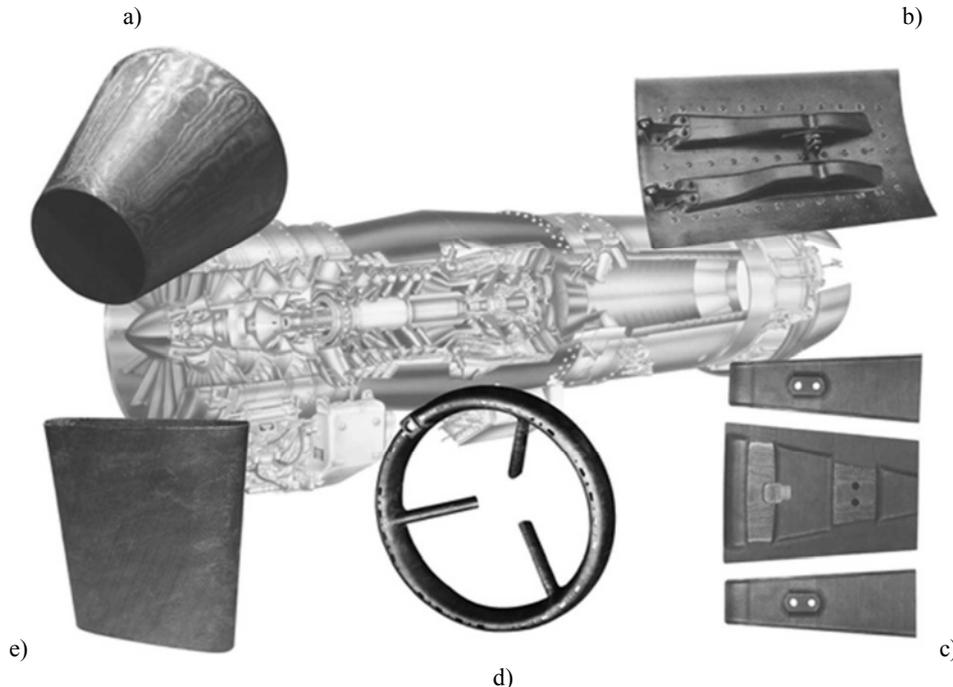


Fig. 7. After-burner parts fabricated with SiC-matrix composites for an aerojet engine: a) exhaust cone, b) outer exhaust nozzle flap, c) inner exhaust nozzle flaps and seals, d) flame holder and e) casing strut, according to F. Christin, ref. [104]

Rys. 7. Części silnika odrzutowego poza komorą spalania: a) stożek dyszy wylotowej, b) zewnętrzna kłapa dyszy wylotowej, c) wewnętrzne kłapy i uszczelnienia dyszy wylotowej, d) stabilizator płomienia, e) element osłonowy, wg F. Christin [104]

There has been during the last decade, a growing interest in the use of CMCs in the field of power generation, such as in cogeneration gas turbines and nuclear reactors. The working conditions of the former and the materials design issues are relatively close to those for an aerojet engine. However, the size is larger, the pressure in the combustion chamber higher and the lifetime longer. The most convincing example of application of CMCs in this domain has been in the design, fabrication and test of large size SiC/SiC liners for combustion chamber [110]. The liners consist of two concentric cylinders (76 and 33 cm in diameter, 20 cm in length and 0.25 cm in thickness), fabricated with BN-coated SiC fibers embedded in a SiC-based matrix and overcoated with an EBC (SiC then multilayered Si/mullite (or mullite + BSAS)/BSAS) in order to improve corrosion resistance. Field tests were conducted on a 4÷5 MW gas turbine with a liner surface temperature of about  $1200^\circ\text{C}$  and accumulated service time of the order of 40,000 hours. This domain might well become one of the main application fields of CMCs at a time when environmental issues (raised e.g. by coal power plants and conventional nuclear fission reactors) are more and more crucial [26, 108, 110-114].

The constraints on the materials are still more severe for CMCs that would be utilized in the nuclear power plants of the future (high temperature fission and fusion

reactors) since the effect of nuclear radiations are added to those of temperature and corrosive atmosphere. An interesting case story is that of the use of SiC/SiC composites for the so-called first wall/blanket of Tokamak fusion reactor through which the heat generated by fusion reactions is extracted with either a pressurized gas (helium) or liquid (Pb-17 Li eutectics) cooling fluid. Here, the materials would experience during long duration a temperature of  $800\div 1000^\circ\text{C}$  in a fast neutron (and other nuclear high energy particles) flux. It has been already shown that SiC/SiC composites, when properly processed (low impurity level constituents, low residual porosity and high thermal conductivity) are actually among the best materials for this application. However, their use in such a harsh

environment raises a number of fundamental issues relevant to solid state physics and materials science (effect of radiations on the structure of and defects formation in SiC, interphase stability, mechanical properties evolution and activation) as well as technical aspects (fabrication of very large parts several meters in size that will have to be assembled, helium or Pb-17 Li hermeticity, joining with low activation brazing alloys), which are extremely challenging and would considerably improve our knowledge of these materials [91-97].

### Braking and friction systems

C/C brakes, which consist of an axial assembly of fixed and rotating disks, are already extensively utilized for military and large capacity civil aircraft. Their use has already been extended to racing cars with a more conventional air-cooled disk/pad configuration. It is presently the most important application of CMCs, in terms of volume production. With respect to conventional steel brakes, their C/C counterparts display a significant weight saving (several 100 kg for a civil airplane of large capacity), more security related to refractoriness and braking performance (in the so-called rejected take off (RTO) conditions, the temperature of C/C brakes can be over 2000°C and the brakes still efficient) and surprisingly longer lifetime. However, C/C brakes are prone to oxidation and moisture effect. Two questions are presently raised in this field: (i) could the performance of C/C brakes be improved by replacing partly or totally the C-matrix by a SiC-based matrix and (ii) could their use be extended to other vehicles (such as trucks, buses, fast trains, etc.), that would tremendously enlarge their market. Preliminary studies suggest that the answers to these two questions might be positive [87-90].

### Other applications

CMCs and more particularly C/C composites have found niche applications in different fields where they are replacing either metal or graphite. Examples are internal equipment for heat-treatment furnaces, susceptor bowls for silicon single crystal growth furnaces or prosthetic devices [73, 98-102, 104]. However, the high cost of ceramic fibers (SiC-fibers), the lack of shared database and design approach (similar to those for metals) and also the novelty of the materials, restrain their utilization in fields where metals are still the reference.

### CONCLUSION

From the analysis presented in previous sections, the following conclusions can be tentatively drawn:

1. Ceramic-matrix composites are non-brittle (damage tolerant) and reliable materials when properly designed and processed.
2. CMCs can be fabricated via a gas phase route (CVI), liquid phase routes (PIP and RMI), or ceramic (powder) route (SIHP). Each of them has its own advantages and drawbacks with a tendency to favor hybrid processes.
3. Three families of ceramic fibers are commonly used as reinforcements: carbon, SiC-based and Al<sub>2</sub>O<sub>3</sub>-based fibers. They are employed as tows, 2D-fabrics or multidirectional preforms. Non-oxide fibers exhibit the best high temperature mechanical properties but are oxidation-prone. Oxide fibers are intrinsically stable in oxidizing atmospheres but they undergo grain growth at moderate temperatures and have a poor creep resistance.
4. An interphase, a few 100 nm in thickness, is commonly used to control FM-bonding and crack deflection. The best interphases seem to be those with a layered crystal structure or microstructure. Porous thin films are a potential alternative.
5. CMCs display a non-linear tensile mechanical behavior related to damaging phenomena, including microcracking, FM-debonding, and fiber pull-out. They are weakly sensitive to notch-effect. CMCs are tough ceramics though their constituents are individually brittle. Their fracture energy is one or two orders of magnitude that of monolithic ceramics. CMCs are resistant to cyclic fatigue. They creep but with a low rate up to 1200÷1400°C (for non-oxide CMCs).
6. C- and SiC-based composites display a good thermal conductivity when their crystallinity is high (after HTT) and their residual porosity low. Conversely, all-oxide composites are insulating materials. Non-oxide CMCs have a low CTE and a high dimensional stability.
7. Non-oxide CMCs are oxidation prone. In a large domain of temperature and oxygen partial pressure, their oxidation is passive, with formation of protecting oxide scales, however, the occurrence of moisture in the environment favors their volatilization. The oxidation resistance can be improved with multilayered coatings (EBCs) or/and self healing matrices.
8. C/C composites exhibit good friction properties at high temperatures but which are depending on moisture absorption. C/C-SiC composites seem to display higher coefficient of friction and lower wear rate, almost independent of the environment.
9. Non-oxide CMCs have several major fields of application: thermal protection of spacecraft, rocket engine nozzles and aircraft braking systems. They are being extended to aerjet engines and gas tur-

bines of cogeneration as well as other braking systems which would considerably enlarge their market.

10. In the future, non-oxide CMCs may find application in other promising domains, such as nuclear reactors and other niches, whereas all-oxide CMCs may become of interest, at medium temperatures (up to 1100°C), for specific applications based on their insulating character and stability in corrosive atmospheres.

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