

Two-dimensional SiC/SiC composites processed according to the isobaric–isothermal chemical vapor infiltration gas phase route

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Abstract

Chemical vapor infiltration (CVI) is a process according to which a ceramic material is deposited from a gaseous precursor in the open pores of a heated substrate. It has been used to elaborate ceramic matrix composites, starting from porous fiber preforms. SiC/SiC composites consist of an SiC CVI-matrix reinforced with Si–C–O ex-polycarbosilane yarn fibers. These composites exhibit non-brittle mechanical behavior in tension loading when a thin layer of a compliant interphase material (turbostratic pyrocarbon or hex-BN) with a low shear failure stress is deposited onto the fibers prior to infiltration of the SiC-matrix. When exposed to oxidizing atmospheres, SiC/C/SiC composites are self healing if their carbon-interphase is thin enough and the temperature is high. Their oxidation resistance can be improved by replacing the vulnerable carbon-interphase by a BN-interphase (low temperature exposures) and/or adding a glass-former coating on the external surface of the composites.

1. Introduction

Ceramic matrix composites (CMCs), consisting of continuous ceramic yarn fibers embedded in a ceramic matrix, exhibit specific features with respect to polymeric or metallic matrix composites. First, they are *inverse* composites, which is to say that the failure strain of the brittle ceramic matrix, ϵ_m^R , is much lower than that of the ceramic fiber ϵ_f^R . Furthermore, the stiffness of the matrix E_m is often of the same order as that of the fiber E_f and sometimes it is even higher. As an example, in SiC-matrix composites reinforced with Si–C–O ex-polycarbosilane (PCS) fibers, $\epsilon_m^R \approx 0.1\%$, $\epsilon_f^R \approx 1\%$, $E_m \approx 400$ GPa and $E_f \approx 200$ GPa [1, 2].

Thus, when a CMC is loaded in tension, the matrix fails first. The challenge is to design the material in such a way that the brittle matrix can undergo extensive microcracking without inducing premature failure of the brittle fibers by notch effects. This is achieved when the fiber–matrix bonding is not too strong. Under such conditions, the matrix microcracks, which usually propagate in mode I perpendicular to the fibers, are deflected in mode II (parallel to the fiber) at the weak fiber–matrix interfaces, turning around the fibers (which become locally debonded from the matrix) instead of continuing their propagation in mode I across the fibers (which is actually what happens when the fiber–matrix bonding is strong). As the load is further increased, the matrix is progressively divided into fragments up to a saturation stage where the spacing between two neighboring microcracks is directly related to

the fiber–matrix bond strength (the spacing being short when the bonding is strong and large when it is weak) [1, 3].

In order to achieve weak enough bonding, two conditions should be fulfilled: (i) no strong chemical bond should be formed between the fiber and matrix during processing and (ii) there should be no residual radial compression stress on the interface, *i.e.* the coefficients of thermal expansion (CTE) have to be properly matched ($\alpha_f^R \geq \alpha_m$) in order to avoid a strong clamping effect on the fiber when the material is cooled from processing to ambient temperatures. The fiber–matrix bonding is usually controlled during processing through the use of an *interphase* (often referred to as the third constituent of the composite) which is a thin layer (typically less than 1 μm) of a compliant material exhibiting a low failure shear stress. Pyrocarbon is the most commonly used interphase material. Unfortunately, it has the drawback of being very sensitive to oxidation even at low temperatures (*i.e.* beyond about 400 °C). Thus, most CMCs with a pyrocarbon interphase have to be protected against oxidation by an *external coating* (*e.g.* a glass-former material such as SiC or Si_3N_4).

To summarize, a tough CMC usually consists of a fibrous reinforcement (*e.g.* carbon or SiC-based fibers) coated with a thin layer of a compliant interphase (*e.g.* pyrocarbon) and embedded in a ceramic matrix (*e.g.* SiC), the whole material being protected by an external coating (such as an SiC-coating). Owing to the extreme damage sensitivity of ceramic fibers (and in some cases

to their limited thermal stability) on the one hand, and to the high melting points and lack of plasticity of ceramic matrices on the other hand, the processing of CMCs has to be performed preferably according to pressureless low-temperature routes, the reinforcements being impregnated (or infiltrated) with a liquid or gaseous precursor of the ceramic matrix. As our strategy, we have selected a gas-phase processing route, chemical vapor infiltration (CVI) [4, 5]. The aim of the present contribution is to describe how tough SiC-matrix composites can be suitably processed by CVI and how they behave under mechanical loading and/or oxidizing atmospheres.

2. Chemical vapor infiltration processing of ceramic matrix composites

2.1. Basis of the chemical vapor infiltration process

CVI has the same chemical basis as low pressure chemical vapor deposition (LPCVD). It has been already the subject of many articles [4–11]. In CVD, a solid (e.g. a ceramic material) is deposited onto a substrate according to a chemical reaction usually involving a mixture of gaseous species referred to as the precursor. Examples of precursors are shown in Table 1: for carbon it can be a hydrocarbon, for SiC a mixture of methyltrichlorosilane (MTS) and hydrogen and for BN a mixture of ammonia and BF₃. The chemical reaction has to be activated; in conventional CVD this is done by heating the substrate at a moderate temperature (at about 1000 °C, i.e. below the melting point of the ceramic deposit).

As shown schematically in Fig. 1, there are three important steps in CVD. The precursor molecules have first to reach the hot substrate surface, then they react together to form the deposit and various gaseous reaction products (such as HCl or HF) and finally the latter have to leave the substrate. Each of these phenomena, i.e. the mass transfer of the reactants or products in the gas phase and the chemical surface reaction, can be rate

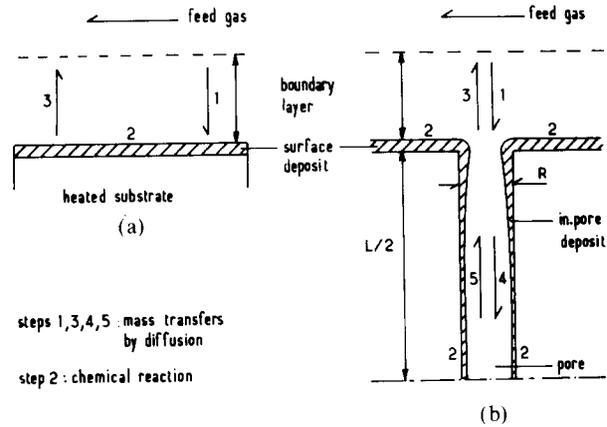


Fig. 1. The different steps in (a) CVD and (b) CVI.

limiting for the overall deposition process depending on the values given to the CVD parameters (i.e. temperature, pressure and gas flow rate) [4–9].

In CVD, the deposit occurs on the external surface of the substrate whereas in CVI, it occurs on both the external surface and in the pores of the substrate. We have shown that lowering the substrate temperature and the total pressure favors the infiltration process [4–7]. Thus, the same process involving the same precursor and the same apparatus can be used either for coating or for infiltration by modifying the deposition parameters.

In our process, *isothermal–isobaric CVI* (or ICVI), the fibrous substrates (referred to as fiber preforms) are set inside a hot-wall isothermal deposition–infiltration chamber (Fig. 2). The mass transfers in the pore network of the substrate occur only by diffusion (Fick and/or Knudsen diffusion depending on the pore geometry and deposition conditions), which is to say that there are no temperature–pressure gradients in the preforms in contrast with the forced CVI-process [11].

Under the conditions mentioned above, the infiltration rate is rather slow (several hundreds of hours being

TABLE 1. Examples of gas precursors and infiltration conditions used for the preparation of various CMCs according to the ICVI process

Matrix	Precursor	Temperature (°C)	Pressure (kPa)
SiC	CH ₃ SiCl ₃ (MTS)–H ₂	900–1100	10–100
B ₄ C	BCl ₃ –CH ₄ –H ₂	900–1000	1–5
TiC	TiCl ₄ –CH ₄ –H ₂	950	1–5
BN	BF ₃ –NH ₃	900–1100	1–5
Al ₂ O ₃	AlCl ₃ –CO ₂ –H ₂	950–1000	2–3
ZrO ₂	ZrCl ₄ –CO ₂ –H ₂	900–940	1–5
Si ₃ N ₄	SiCl ₄ –NH ₃	900–1000	

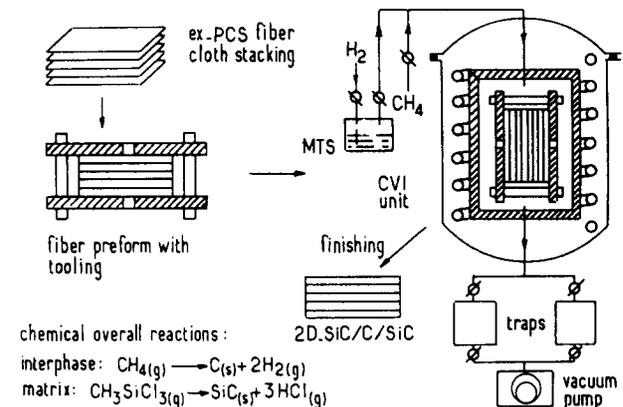


Fig. 2. The isothermal–isobaric CVI process (ICVI) used to elaborate SiC-matrix composites with a carbon interphase from a two-dimensional fiber preform.

necessary to fill almost totally the open porosity of the fiber preforms) but a large number of preforms (which can eventually be different in size and shape from one another) are treated simultaneously, giving a high flexibility to the process. Finally, since the infiltration becomes more and more difficult as the pore size decreases, it is usually stopped when the overall residual porosity is of the order of 10%–15% (the residual porosity being higher in the center of the preform than near the external surface).

2.2. Processing of two-dimensional SiC/SiC composites

The processing of the so-called SiC/SiC composites from Si–C–O (ex-PCS) ceramic fibers according to the ICVI route involves four main steps.

2.2.1. The fiber preform

A fiber preform is first elaborated, usually from continuous multifilament yarns, whose nature and shape are directly related to those of the part and to the applied load pattern. In order to exhibit high infiltration ability, the preform must have a high open porosity (network of interconnected pores) with a pore spectrum characterized by a high fraction of large-diameter pores (diameters ranging from 10 to 500 μm). These large-diameter pores remain open for a long time as infiltration proceeds and are used for mass transfer of the reactants–products whereas the small pores (diameters less than 10 μm) are rapidly filled with the deposit.

Two-dimensional (2D) preforms, consisting of a stack of ceramic fiber cloths kept pressed together with tooling (to adjust the fiber volume fraction V_f in the composite) are often used with the following advantages: (i) such preforms exhibit high infiltration ability, (ii) most ceramic fibers are available as cloths, and (iii) many parts in aerospace applications are thin (Fig. 2). However, in a few cases a third direction of reinforcement (referred to as direction 3, directions 1 and 2 being the warp and woof directions of the cloths) is necessary and three-dimensional preforms are used.

Si–C–O fibers (*e.g.* Nicalon fibers from Nippon Carbon, Tokyo), obtained from a molten polycarbosilane precursor, according to a spinning–oxygen-curing–pyrolysis process, are the most commonly used reinforcements in CMCs [12, 13]. It should be mentioned that such fibers, which are either amorphous or poorly crystallized, have limited thermal stability. Beyond about 1100 $^{\circ}\text{C}$, they undergo decomposition–crystallization with evolution of gaseous species (SiO and CO), a change in surface composition and a significant decrease in mechanical properties [13]. Thus, for very high temperature applications, Si–C–O (ex-PCS) fibers should be replaced by the more stable carbon fibers.

2.2.2. Infiltration of the interphase

In a second step, the interphase material (pyrocarbon or hexagonal-BN) is deposited by ICVI in the preform at about 1000 $^{\circ}\text{C}$ and under a low pressure (a few kilopascals or 10 kPa), its thickness being in the range 0.1–1 μm . It has been shown that the pyrocarbon or BN interphase films are turbostratic nanoporous layered materials [14–17]. The hexagonal layers are randomly oriented in the bulk but tend to be aligned parallel to the fiber surface very near that surface (*i.e.* over about 10 nm) in tough CMCs. Since the interphase has to be formed at a low temperature (a requirement of the ICVI process), it might exhibit defects and contain impurities. As an example, the BN-interphase deposited at approximately 1000 $^{\circ}\text{C}$ from $\text{BF}_3\text{--NH}_3$ is non-stoichiometric ($[\text{N}]/[\text{B}] \approx 0.75$ (atomic ratio) instead of 1) and contaminated with oxygen (approximately 15 at.%), in the as-infiltrated state (the oxygen contamination probably arises from some outgassing of moisture from the apparatus).

2.2.3. Infiltration of the SiC matrix

In a third step, the SiC ceramic matrix is infiltrated in the open pores of the preform still present after the interphase infiltration. As infiltration proceeds, the mean pore diameter becomes smaller and smaller, the deposition of the matrix becoming more and more difficult and time consuming. When the infiltration conditions are not perfectly optimized (or when it has been chosen deliberately to increase the deposition rate at the expense of homogeneous infiltration), the pore entrances can become prematurely plugged. Under such conditions, the external surface of the preform has to be machined in order to re-open the pores. The infiltration process is usually stopped when the overall residual porosity is of the order of 10%–15%. As a result, 2D-SiC/SiC composites exhibit rather large residual pores which are located between the almost fully infiltrated fiber tows (whose porosity consists of only very small pores, usually closed). The intertow large pores have an angular cross-section; they play an important role in the initiation process of the matrix microcracking and in the diffusion of oxygen when the material is loaded in tension or aged in air at high temperatures.

The nature of the interphase, as can be observed *e.g.* by high resolution transmission electron microscopy (HR-TEM) and/or Auger electron spectroscopy (AES) microanalysis, should be discussed at this step of the processing procedure. The infiltration of the SiC-matrix by ICVI requires a rather long time (typically a few hundreds of hours for a 2D preform). Since it occurs at a rather high temperature (*i.e.* around 1000 $^{\circ}\text{C}$), it might act as an annealing treatment with two possible effects: (i) a change in the composition and/or structure

of the interphase material and (ii) a change in the surface nature of the Si–C–O (ex-PCS) fibers. As an example, the BN-interphase deposited from $\text{BF}_3\text{--NH}_3$ tends to become stoichiometric and its oxygen content falls below 5 at.% during the long SiC ICVI step [14]. Conversely, the infiltration temperature is too low to induce a significant change in the structure of both the carbon and BN interphases which remain mainly turbostratic (graphitization starting beyond 1800–2000 °C for BN). As an example of the second effect (ii), an additional interphase consisting of a C/SiO₂ double layer located between the Si–C–O (ex-PCS) fiber and the carbon or BN-interphase deposited in step 2, is often observed in SiC/SiC composites processed by ICVI, the interfacial sequences being Si–C–O(fiber)/C/SiO₂/C(interphase)/SiC(matrix) or Si–C–O(fiber)/C/SiO₂/BN(interphase)/SiC(matrix). This C/SiO₂ double layer is amorphous, each of the sublayers having a thickness of a few nanometers (or a few tens of nanometers). This C/SiO₂ double layer might have two origins: (i) it could be formed from impurities present on the Si–C–O(ex-PCS) fibers before step 2 and/or (ii) it could result from some decomposition of the amorphous Si–C–O phase of the fibers, occurring during the long ICVI steps 1 + 2 (Fig. 3). The weakest link in the interfacial phase sequence has been reported to be at or very near the silica amorphous layer when the C/SiO₂ double layer is actually present, *e.g.* in 2D-SiC/BN/SiC composites (Fig. 4) [15]. It thus appears that the role played by the interphase in CMCs could be more complex than initially thought. Tentatively, the interphase deposited in step 2 might

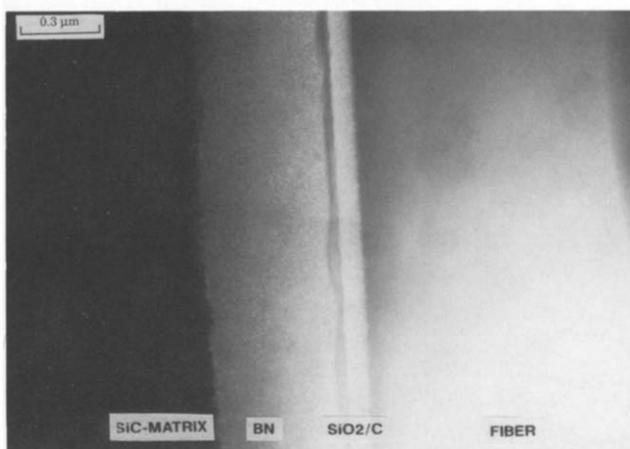


Fig. 3. Transmission electron micrograph (bright field) of the interfacial sequence in an SiC/SiC composite elaborated from Si–C(O)ex-PCS fibers according to the ICVI process; the BN-interphase was deposited from $\text{BF}_3\text{--NH}_3$ and the SiO₂/C amorphous double layer was formed *in situ* during processing [14].



Fig. 4. Mode-I–mode-II deflection of a matrix microcrack at or near the amorphous silica layer in a 2D-SiC(O)fiber/BN/SiC composite (transmission electron micrograph, bright field image) [14].

(i) provide a weak interface with a low shear failure stress and a low coefficient of friction when it has been debonded (this interface could be either one of the interfaces involving the amorphous silica sublayer or that between two well oriented carbon or BN adjacent hexagonal layers) and (ii) act as a compliant buffer to relax the residual normal compression stress generated on the fiber when the material is cooled from processing to room temperatures (in Si–C–O(ex-PCS)fiber/SiC(CVI)matrix, the CTE of the matrix is slightly higher than the radial CTE of the fibers). These two assumptions would be consistent with the fact that the achievement of good mechanical properties requires a thick enough carbon (or BN) interphase [15].

2.2.4. Deposition of an external coating

As already mentioned, a CMC with a constituent sensitive to oxidation (*i.e.* a carbon interphase and/or carbon fibers) has to be protected with an external coating when it is exposed to oxidizing atmospheres at high and even medium temperatures. Such a coating, which usually consists of a glass-former material (*e.g.* SiC or Si₃N₄), is deposited by CVD in the last step of the process.

It thus appears that one of the advantages of the gas phase route lies in the fact that three important steps of the process (steps 2, 3 and 4) can be performed with the same technology and eventually with the same apparatus, the flexibility of the process mitigating the somewhat long infiltration times.

3. Mechanical behavior and effect of environmental parameters

3.1. Mechanical behavior at room temperature

The mechanical behavior of 2D-SiC/SiC composites in tension (load applied along directions 1 or 2) is strongly dependent on the nature of the fiber–matrix chemical and mechanical bonding. When this bonding is strong, *e.g.* when no interphase has been deposited onto the fiber surface (step 2 omitted), the material behaves in a brittle manner: the first cracks initiated in the matrix propagate in mode I (perpendicular to the fiber axis along which the load is applied) and break the unprotected fibers by notch effects. Under such conditions, the failure of the matrix results in that of the composite at a low strain (less than 0.1%) and with no fiber pull-out.

Conversely, when a compliant interphase has been deposited onto the fibers prior to the SiC CVI step, the composite exhibits non-linear stress–strain behavior related to the occurrence of various damaging phenomena, including matrix microcracking, fiber–matrix debonding, friction of the debonded broken fibers against the matrix and fiber pull-out. However, the material remains elastic in a first approximation up to failure, as supported by the results of tests performed under unloading–reloading cycles. Thus, 2D-SiC/SiC composites are often depicted as *linear-elastic damageable* materials [18].

The shape of the stress–strain tensile curves and the extent of the non-linear domain depend on the nature of the fiber–matrix interfacial zone, as shown recently by Prouhet *et al.* for 2D-SiC/BN/SiC composites [15] and by Cojean for 2D-SiC/C/SiC composites [19] (Fig. 5). When the interphase deposited in step 2 is too thin (*e.g.* 0.1 μm or less) (i) the non-linear σ – ε domain is narrow, (ii) failure occurs at a low strain (typically 0.2%) and with limited fiber pull-out, and (iii) the spacing of the matrix microcracks is short, suggesting very good load transfer. These features correlate well

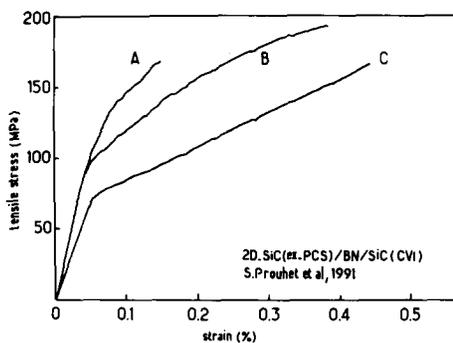


Fig. 5. Tensile stress–strain curves at room temperature of 2D-SiC(O) fiber/BN/SiC composites with BN-interphases of increasing thicknesses (A, 0.15 μm ; B, 0.50 μm and C, 2.7 μm) [15].

with the HR-TEM images which show that under such conditions, the interphase deposit is too thin (*i.e.* step 2 is too short) to give rise to a continuous low failure shear stress interface lying parallel to the fiber surface. Thus, the fibers are not well enough protected, the residual compression axial stresses cannot be properly relaxed and the matrix microcracks are not systematically and easily deflected from mode I to mode II, with the result that the composite fails prematurely (curve A in Fig. 5).

Conversely, when the interphase is thick enough and/or when its microstructure is well enough ordered (i) the non-linear σ – ε domain is large, and (ii) failure occurs at a strain which is high for a ceramic material (0.5%–0.6% and even 0.8%–1%) with significant fiber pull-out. Furthermore, two kinds of non-linear σ – ε domain shapes have been reported for both 2D-SiC/BN/SiC and 2D-SiC/C/SiC. The first shows an inflexion (see curve C in Fig. 5) or even a quasi-plateau before failure, which correlates with a large spacing of the matrix microcracks (the microcracking saturation stage being achieved near that inflexion, *i.e.* well before failure) thus suggesting low fiber–matrix bonding. Such a situation has been observed for 2D-SiC/BN/SiC composites with a thick BN-interphase ($e > 1 \mu\text{m}$) where a continuous C/SiO₂ double layer was present (Fig. 6) [15]. The second does not exhibit such an inflexion (or quasi-plateau), the stress increasing monotonously as the material is progressively strained up to failure. Such

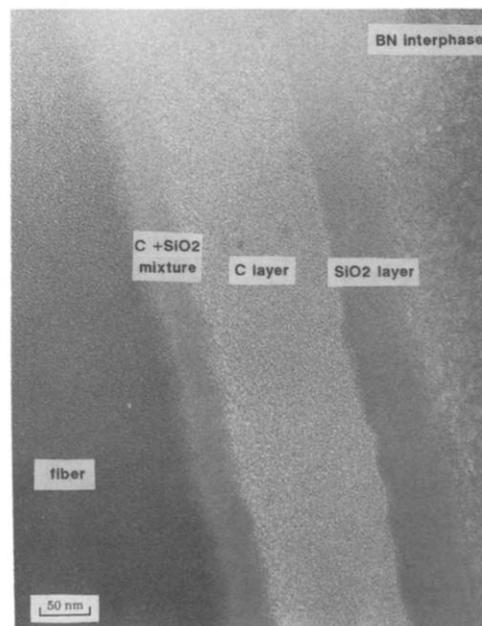


Fig. 6. Transmission electron micrograph (bright field) of the interfacial phase sequence showing the continuous C/SiO₂ amorphous double layer in a 2D-SiC(O) fiber/BN/SiC composite (material B of Fig. 5) elaborated by ICVI [15].

behavior could be related to a stronger fiber–matrix bonding as supported by a shorter spacing of the matrix microcracks, the microcracking saturation being reached near failure. 2D-SiC/BN/SiC with an intermediate thickness of BN-interphase behaves in such a manner (curve B in Fig. 5).

3.2. Effects of environmental parameters

3.2.1. Oxidation kinetics of SiC/SiC composites

The oxidation of Si–C–O(ex-PCS)fiber/C-interphase/SiC matrix composites has been studied on one-dimensional model materials (all fibers in one given direction) with two carbon interphase thicknesses ($0.1\ \mu\text{m}$ for material D and $1\ \mu\text{m}$ for material E) [20]. When the material is aged in oxygen or air (under test conditions corresponding to the so-called passive oxidation of SiC, *i.e.* medium temperatures and high oxygen partial pressures), the following chemical phenomena occur: (i) the carbon interphase is consumed over a certain length with the evolution of carbon oxides, weight loss and the formation of an annular pore around each fiber, whose size is equal to the interphase thickness and (ii) the oxidation of the pore wall resulting in the growth of two silica layers with a weight increase (Fig. 7).

From thermogravimetric analysis (TGA) experiments and numerical simulations, it appears that the oxidation of the carbon interphase is rate limiting at the beginning of the oxidation process, the weight loss being directly related to the thickness of the carbon interphase (Fig. 8). Later, oxidation is rate controlled by the diffusion of oxygen along the annular pores, part of the oxygen reacting with the pore wall to give silica with a weight increase. When the thickness of the carbon interphase is low ($0.1\ \mu\text{m}$) and the temperature is high ($1200\text{--}1400\ ^\circ\text{C}$), silica plugs the annular pores very rapidly and the oxidation process is stopped (or at least greatly slowed down). Under such conditions, the composite is self healing. Conversely, when the carbon interphase is thick ($1\ \mu\text{m}$) and the temperature is low

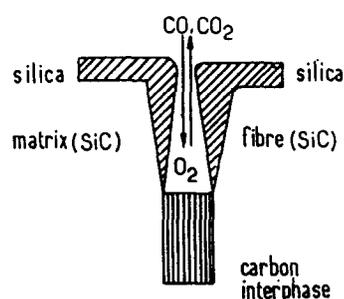


Fig. 7. Chemical phenomena involved during the oxidation of an SiC/C/SiC composite [20].

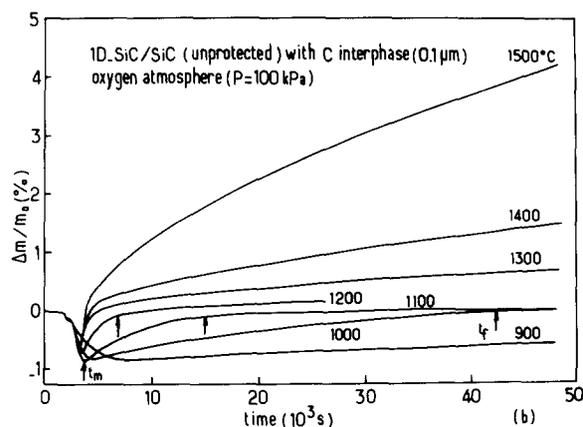


Fig. 8. Thermogravimetric analysis curve of 1D-SiC/C/SiC model composites with a thin carbon-interphase ($e = 0.1\ \mu\text{m}$, material D) exposed to a pure oxygen atmosphere at various temperatures [20].

($400\text{--}1000\ ^\circ\text{C}$), the growth rate of silica is slow, the pores remain open and in-depth oxidation occurs.

Since the oxidation of BN starts at $800\text{--}900\ ^\circ\text{C}$ whereas that of carbon is already effective at $400\text{--}500\ ^\circ\text{C}$, replacing the carbon-interphase by a BN-interphase is thought to improve the oxidation resistance of SiC/SiC composites at low temperatures. Furthermore, the use of a glass-former coating (*e.g.* SiC or Si_3N_4) deposited onto the external surface of the composites impedes (or at least slows down) the diffusion of oxygen towards the vulnerable carbon interphase.

3.2.2. Effect of oxidation on mechanical behavior

Generally speaking, oxidation treatment may have three different effects on the mechanical behavior of SiC/C/SiC composites [20, 21]. First, when it is performed at a low temperature (*e.g.* $400\text{--}800\ ^\circ\text{C}$), on a composite with a thick enough interphase, the carbon interphase is consumed and the fibers are no longer bonded to the matrix. Thus there is no longer any load transfer. Second, when the interphase is thinner and the temperature higher, the weak fiber–matrix bonding through the carbon-interphase is replaced by a strong bonding through silica and a tough–brittle transition is expected. Finally, at very high temperatures (beyond $1200\ ^\circ\text{C}$ and for long exposures), the metastable Si–C–O fibers undergo decomposition process with loss of strength.

Tests performed on unprotected 1D-Si–C–O/C/SiC model composites have shown that the best results, in terms of oxidation resistance and retention of mechanical properties at room temperature after ageing in air, were observed for oxidation ageing at high temperatures and for composites with a thin carbon interphase (Fig. 9). Under such conditions, oxidation is limited to near the external surface of the composite and its effect on the mechanical behavior is limited (the strength

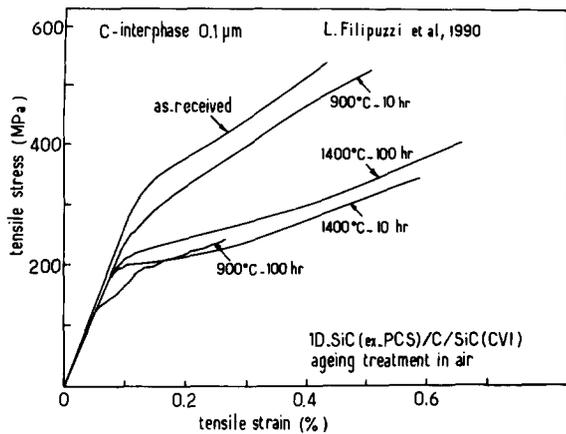


Fig. 9. Tensile stress-strain curves recorded at room temperature for 1D-Si-C(O) fiber/C/SiC model composites with a thin carbon-interphase (material D) after ageing treatments in air at 900 and 1400 °C [20].

decrease could be related to some decomposition of the fibers, as mentioned above) [21].

Tests performed on 2D-Si-C-O/C/SiC composites with an external coating show that such materials can be used in oxidizing atmospheres (passive oxidation) up to about 1200 °C for rather long durations (e.g. several tens of hours) [22].

4. Conclusions

(i) Tough CMCs have been elaborated from Si-C-O(ex-PCS) yarn fibers bonded to an SiC-matrix through compliant pyrocarbon or hex-BN interphases with a low shear failure stress.

(ii) ICVI appears to be a processing route well suited to the manufacture of parts of large size for aerospace structural applications, owing to its high flexibility.

(iii) SiC/C/SiC and SiC/BN/SiC composites behave as non-brittle damage-tolerant materials; they exhibit a non-linear stress-strain domain in tension, the extent of which is directly related to the nature of the fiber-matrix bonding.

(iv) SiC/C/SiC composites have rather good oxidation resistance as long as their carbon interphase is not too thick and the temperature is high enough, owing to the formation of a protective layer of silica (self-healing materials). It can still be improved by replacing the carbon-interphase by a BN-interphase and by adding an external coating.

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