Silicon Carbide and Carbon Composites

SINGLE- AND MULTI-LAYERED INTERPHASES IN SiC/SiC COMPOSITES EXPOSED TO
SEVERE CONDITIONS: AN OVERVIEW

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ABSTRACT
        Pyrocarbon (PyC), which is presently the best interphase material for SiC/SiC composites is not stable
under conditions encountered in advanced applications: it is sensitive to oxidizing atmospheres or to neutron
irradiation, even at moderate temperatures. Attempts have been pursued to replace PyC-interphase by boron
nitride, which is more resistant to oxidation but poorly compatible with nuclear applications. Other interphase
materials, such as ternary carbides (MAX-phases) seem promising but their use in SiC/SiC has not been
demonstrated. Hence, the most efficient way to improve the behavior of PyC-interphase in severe environments
is presently to replace part of the pyrocarbon by a second material displaying a better compatibility with the
environment, such as SiC itself ((PyC-SiC)$_n$ multilayered interphases). Important issues related to the design and
behavior of layered interphases are reviewed on the basis of LCTS-experience and recent data published by
others with a view to demonstrate their potential interest in HT-nuclear reactors.

1-   INTRODUCTION
        The interphase plays a key role in the behavior of ceramic matrix composites (CMCs). It
prevents the early failure of the fibers, matrix microcracks being arrested or/and deflected parallel to
fiber axis (so-called "mechanical fuse" function). It also transfers load from the fibers to the matrix and
eventually releases part of residual thermal stresses. The interphase protects fibers against chemical
reactions that could occur during processing and use of CMCs in aggressive environments.
        It has been postulated, that the best interphase materials for SiC/SiC might be those with a
layered structure, the layers being parallel to fiber surface, weakly bonded to one another but strongly
adherent to fibers [1-4]. It appeared that pyrocarbon was the best interphase material for SiC/SiC in
terms of their mechanical behavior [1-5].
Unfortunately, pyrocarbon is oxidation prone even at low temperatures with the result that PyC-
interphase can be consumed and the FM-coupling lost. Hence, that interphase becomes the weak point
of SiC/SiC when used in *oxidizing atmospheres* (gas turbines). Within the same conceptual framework,
two alternatives have been proposed: boron nitride (BN) and (X-Y)$_n$ multilayers. The former displays a
structure similar to that of graphite while being more oxidation resistant [5-7]. In the latter, with X =
PyC or BN, Y = SiC and n = 1 to 10, part of the oxidation prone X-constituent is replaced by a material
Y exhibiting a better oxidation resistance, such as SiC itself [1-4, 8-12]. Furthermore, this concept of
material multilayering has been extended to the matrix, yielding "self-healing" composites with
outstanding lifetimes in oxidizing atmospheres [10, 13, 14].
        More recently, SiC/SiC composites have been envisaged as structural materials in high
temperature nuclear reactors. The interphase appears again as a possible weak point, PyC being known
to undergo volume change when exposed to neutrons whereas BN undergoes nuclear reactions [15-17].
Research is presently pursued following two similar routes: (i) use of thin single PyC-layers and (ii)
use of (PyC-SiC)$_n$ multilayers, to minimize the effect of neutron irradiation [15-21].
        The aim of the present overview is to recall the basis of the layered interphase concept, to
discuss its application to SiC/SiC exposed to oxidizing environment and tentatively, to neutron
irradiation.

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2- PYROCARBON SINGLE LAYER INTERPHASE: THE REFERENCE

Pyrocarbon has a structure similar to that of graphite but the elementary graphene layers are of limited size and stacked with rotational disorder. Our layered interphase concept requires that: (i) the layers should be oriented parallel to fiber surface and (ii) the bonding between the fiber and the PyC-interphase should be strong enough. Otherwise, debonding/crack deflection would occur at the fiber surface exposing the fiber to mechanical damage and to the atmosphere [3, 4].

2.1- Pyrocarbon texture

Pyrocarbon displays a variety of microtexture and anisotropy, which can be characterized by optical microscopy in polarized light (extinction angle, A_e) or/and transmission electron microscopy (L_2, N parameters): the larger A_e, the higher the anisotropy [22]. The preferred PyC for an interphase is *rough laminar* ($A_e > 18°$) This RL-PyC has a tendency to grow with graphene layers parallel to fiber surface. It is usually deposited by CVI (I-CVI or P-CVI) from propane or propylene [1, 5, 9, 23].

2.2- Fiber/PyC-interphase bonding

The second requirement is a strong-bonding between the fiber and the PyC-interphase [3, 4]. Achieving such a strong bonding is first a matter of surface chemistry. The surface of desized Si-C-O fibers (Nicalon) is enriched in oxygen and free carbon. As a result, there is in SiC/SiC (CVI) a thin and irregular dual layer of amorphous silica and carbon which introduces a weak link near the fiber surface [1, 3-6, 24, 25]. The fibers should be pretreated to clean their surface and achieve a strong FI-bonding. Another example is the SiC + C fibers (Hi-Nicalon), whose microstructure is not fully stabilized after processing and whose surface may also contain some oxygen. During CVI-processing, fibers undergo a post-shrinkage weakening the FI-interface. Again, the fibers should be pretreated. Finally, stoichiometric SiC fibers (Hi-Nicalon type S, HNS, or Tyranno SA, TSA), fabricated at higher temperatures are assumed to be dimensionally stable at composite processing temperatures. Further, their surface consists of free carbon (resulting from SiC decomposition) [26]. Hence, their bonding with PyC-interphase is expected to be relatively strong.

Finally, the roughness of fiber surface, which is low for Nicalon and Hi-Nicalon but significant for stoichiometric fibers, adds a mechanical contribution to the FI-bonding in a transition zone where the nanometric graphene layers stacks become progressively parallel to fiber axis [1, 7].

2.3- SiC (Nicalon)/PyC/SiC: a case history

Studies on SiC/PyC/SiC (CVI) fabricated with Nicalon or Hi-Nicalon fibers (as-received or pretreated), clearly show the positive effect of FM-interfacial design on material properties [1-4]. As shown in Fig. 1, tensile curves for the composites with a single 500 nm PyC-interphase (samples I and J) exhibit extended non-linear domains related to damaging phenomena, with high failure strains. However, composite with pre-treated fibers (sample J) is much stronger.
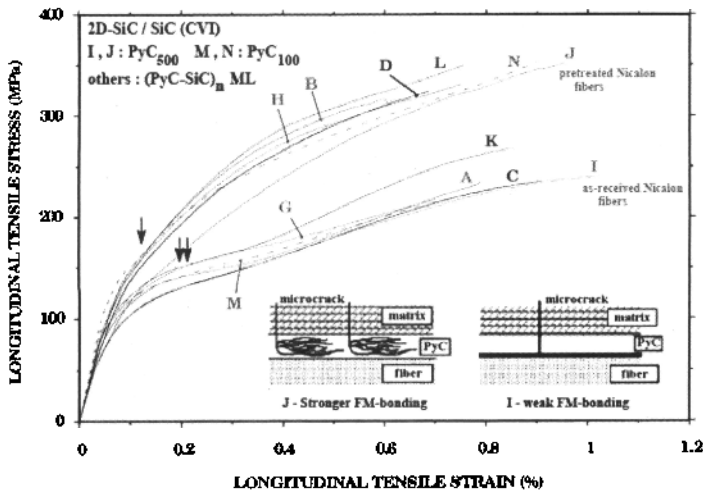
Fig. 1: Tensile curves at ambient of 2D-SiC/SiC (CVI) fabricated from Nicalon fibers with different interphases: single PyC-layers or (PyC-SiC)n ML-interphases (adapted from ref. [1]).

The shapes of the curves are different: continuously convex for the composite with pretreated fibers (sample J) and with a plateau-like feature for that with as-received fibers (sample I). Matrix microcracks are deflected near fiber surface (I-inset, right) for the latter, at the level of the weak carbon/silica interface and within the PyC-interphase (in a diffused manner and over short distance, J-inset, left) for the former. Here, the PyC-interphase does play its role of mechanical fuse. These two microcrack deflection modes correspond to very different FM-coupling, (weak in I and stronger in J). Interestingly, toughness of the composites fabricated with pretreated fibers as well as their fatigue resistance in tensile cyclic loading are higher when it is the PyC-interphase which is the active mechanical fuse (strong bonding) [1, 2, 27]. Similar results have been reported for composites fabricated from Hi-Nicalon fibers and PyC-interphase.

2.4- Influence of PyC-interphase thickness

PyC-layer thickness, e(PyC), has an influence on the mechanical properties of SiC/PyC/SiC composites, through thermal residual stresses (TRS) and fiber surface roughness.

In SiC/PyC/SiC (CVI) fabricated at $\approx 1000°C$ using Nicalon or Hi-Nicalon fibers, the coefficient of thermal expansion of the fibers is lower than that of the matrix, which results in compressive radial TRS at the FM-interface and reinforces FM-bonding. Further, the fiber surface is very smooth. Hence, increasing e(PyC) relaxes radial compressive TRS and lower interfacial shear stress. Experimental studies have shown that the mechanical properties go through an optimum for e(PyC) = few 100 nm [11, 15, 28]. P. Dupel et al. have reported that the tensile properties of 1D-SiC (NCG)/PyC/SiC (P-CVI) minicomposites were optima for e(PyC) = 220 nm. The calculated radial TRS in the interphase was compressive (enhancing thus the FM-bonding) at low e(PyC) values and tensile (favoring FM-debonding) for e(PyC) > 400 nm [29].

In SiC/SiC fabricated with stoichiometric fibers, the situation is different since the CTEs of the main constituents are now similar but the fiber surface is highly crystalline and rough. The mechanical properties of 2D-SiC/PyC/SiC (CVI) are either constant or slightly dependent on interphase thickness,

when e(PyC) increases from 25 to 250 nm [17, 30]. As it could be expected from fiber roughness, the interfacial frictional stress τ_f is higher for composites with Tyranno fibers than for those with Hi-Nicalon fibers and decreases as e(PyC) increases [12].

2.5- Crack deflection modeling

Crack deflection at an interface in brittle materials has been modeled [31, 32]. Recently, S. Pompidou and J. Lamon have proposed a model, derived from the approach of J. Cook and J.E. Gordon [32], which is applicable to composites with single- or multi-layered interphases [33, 34]. When a crack of tip radius ρ is placed in an elastic medium and subjected to a uniaxial tension σ_{zz} (in a direction z perpendicular to crack plane), it generates a multiaxial stress field near crack tip of which σ_{rr} component (in radial direction) is maximum at a distance on the order of ρ ($\sigma_{rr}^{max} = \sigma_{rr}(r = \rho)$). If an interface is placed perpendicular to primary crack extension direction near crack tip, a secondary local crack may nucleate at that interface if $\sigma_{rr}^{max} > \sigma_i^c$, where σ_i^c is the interface debonding stress. Deflection results from coalescence of both cracks [32]. When applied to a microcomposite loaded in tension along fiber axis, debonding would occur when: $\sigma_i^c / \sigma_f^c \leq \sigma_{rr}^{max} / \sigma_{zz}^{max}$ (with $r > \ell$) , where σ_f^c is the failure stress of the fiber and, ℓ the distance between crack tip and interface (or ligament) [33, 34]. σ_{rr}^{max} and σ_{zz}^{max} were computed and their ratio plotted vs the Young's moduli ratio E_2/E_1, as shown in Fig. 2. The domain under this master curve corresponds to the debonding situation and that above to conditions where debonding cannot occur. The curve exhibits a maximum corresponding to the highest debonding potential. Conversely, when E_2/E_1 decreases and tends to zero, debonding becomes quite impossible. But, the crack can be arrested. Failure of the reinforcing material depends on its strength versus stress operating: σ_f^c vs σ_{zz}^{max} .

The model has been applied to SiC/PyC/SiC to examine crack deflection probability at a given interface or within the interphase, to show the influence of fiber pretreatment and to discuss the effect of graphene layer orientation in the interphase. Deflection at first interface (SiC$_m$/PyC$_i$) is very unlikely since for the related E_2/E_1 ratio (≈ 0.07), the value of σ_i^c should be extremely low (Fig. 2) in accordance with experiments. By contrast, deflection at second interface (PyC$_i$/SiC$_f$) is most likely since for the corresponding E_2/E_1 ratio (10 for Hi-Nicalon) the width of the debonding domain (debonding potential) is very large. This is the most frequently observed case (weak FM-bonding). If the fiber has been pretreated to strengthen the FM-bonding, the representative point may move above the master curve, with debonding no longer occurring at that interface. However, it may take place within the PyC-interphase, i.e. at a PyC$_i$/PyC$_i$ interface which shows for a E_2/E_1 value of 1, a still significant deflection potential (Fig. 2). This is the situation observed, for pretreated Nicalon fiber [1-4]. If now the graphene layers are deposited perpendicular to fiber surface, crack deflection within the PyC-interphase becomes no longer possible since the ratio $\sigma_{PyC//}^c / \sigma_{PyC\perp}^c \approx 2.17$ is well above the master curve for $E_2/E_1 = 1$.
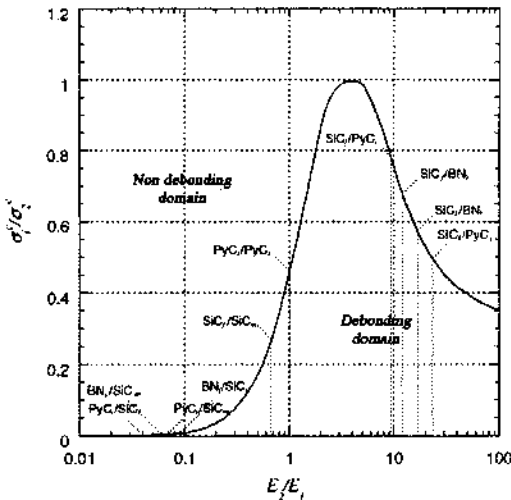
Fig.2: Values of σ_1^c / σ_2^c ratio provided by the master curve for various fiber/matrix and fiber/interphase/matrix systems (cracked material (material 1) cited second) (adapted from ref. [34]).

3-   LAYERED INTERPHASES FOR SiC/SiC EXPOSED TO OXIDIZING ATMOSPHERE

Pyrocarbon is oxidation prone even at temperature as low as $\approx 500°C$, its oxidation resulting in the formation of gaseous oxides (active oxidation) and degradation of FM-coupling [35, 36]. Two approaches have been selected to solve this problem relying on self-healing (or self-sealing) mechanisms by condensed oxides (passive oxidation). The first one is based on single layer interphases containing boron whereas in the second, part of PyC is replaced, in so-called multilayered interphases, by SiC or TiC to reduce the thickness of each elementary PyC sublayer to a few 10 nm and to favor self-healing phenomena [9, 10].

3.1- Boron-doped pyrocarbon interphase

The addition of boron to pyrocarbon increases its graphitic character at low B-concentration and improves its oxidation resistance by blocking the so-called active sites and forming a fluid oxide (B_2O_3) in a temperature range (500-900°C) where the growth kinetics of silica is still too slow [37].

S. Jacques et al. have studied the influence of B-doped PyC-interphase on the oxidation resistance of 1D-SiC/SiC (CVI) microcomposites with pretreated Nicalon fibers [38]. Their interphases contain up to 30 at.% B. They showed, as expected, that the microtexture of the PyC-interphase was significantly improved at low B-addition, 8 at.% B, and degraded beyond this value (the interphase becoming amorphous). More importantly, lifetime in tensile static fatigue (beyond PL) in air at 700°C was dramatically improved as the B-content was raised, the best results being observed for graded interphase. Crack deflection and failure occur within the interphase at a location where the interphase microtexture and graphene layer orientation were optimal (at ≈ 8 at. % B).

3.2- Boron nitride interphases

The use of BN-interphase in SiC/SiC raises several problems which still remain imperfectly solved. They include the occurrence of corrosion by precursor and the chemical reactivity of BN with oxygen and moisture when prepared at low temperature.

3.2.1- BN-interphases as deposited by CVI from BF_3-NH_3

BF_3-NH_3 precursor has the advantage of yielding well-crystallized BN deposits at relatively low temperature [6, 39]. Unfortunately, it involves gaseous species (BF_3 and HF) which are corrosive for SiC-based fibers and alter their strength (as received Nicalon and Hi-Nicalon) [40]. Conversely, this precursor is compatible with carbon substrates and it could be used to deposit BN on fibers with a carbon layer surface (pretreated or stoichiometric fibers) [41]. However, an extra carbon layer usually remains between the fiber and the BN-coating which could be the weakest link in the interfacial zone.

One way to solve the corrosion problem and to play with the mechanical fuse location could be to deposit BN in a temperature gradient (TG-CVI). S. Jacques et al. have fabricated 1D-SiC/BN/SiC minicomposites with a radial crystallinity gradient by simply passing a Hi-Nicalon tow through a 3-temperature zones furnace [42]. Under optimized conditions, in terms of fiber progression speed, the FM-bonding was strong (crack deflection occurring within BN-interphase (Fig. 3)) and both interfacial shear stress and tensile stress were high. At lower fiber speed, crack deflection occurred at fiber surface (as a result of some surface crystallization) whereas for higher fiber speed it was observed at the SiC_m/BN interface, these two scenarios corresponding to the "inside" and "outside" debonding reported by G.N. Morscher et al., in related experiments [43]. In the case of "outside" debonding, both the interfacial shear stress and tensile failure stress were lower but the lifetime in tensile static fatigue at 700°C in dry or wet air was dramatically improved (crack deflection occurring far from fiber surface) [42].

3.2.2- BN-interphases as deposited by CVI from BCl_3-NH_3-H_2

BCl_3-NH_3-H_2 precursor is usually preferred since it is much less corrosive [44-47]. In principle, BN could be deposited at temperature as low as 700°C. However, under such mild conditions, it is nanoporous, poorly organized and highly reactive. Hence, the processing temperature should be increased [5, 44-47]. In the case of complex fiber architectures (nD-preforms), BN can be deposited at the highest temperature compatible with the ICVI-process ($\approx$ 1100°C) and further annealed at a temperature corresponding to the upper limit of the thermal stability domain of the fibers. An alternative is to deposit BN on fiber *tows*, which can be done at higher temperature (1400-1600°C), particularly for stoichiometric SiC-fibers [48]. As an example, BN deposited on a Tyranno SA tow at 1580°C was reported to be nearly stoichiometric, with an impurity content less than 5 at. %, highly crystallized and textured [49]. Another efficient way to improve the oxidation resistance of BN is to dope the precursor with a silane. The resulting BN(Si) deposit (15-40 wt. % Si), displayed an oxidation rate (at 1200-1500°C) 2-3 orders of magnitude lower than that for undoped BN [50]. Unfortunately, such Si-doped BN is amorphous and hence at variance with the first requirement of our layered interphase concept.
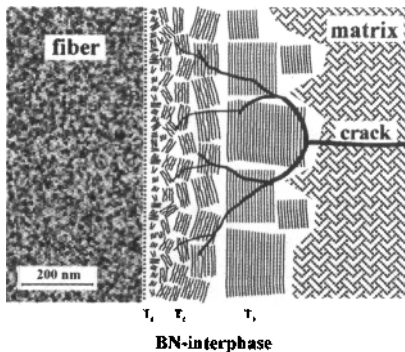
BN-interphase
Fig. 3: BN-interphase deposited from BCl_3-NH_3-H_2 on Hi-Nicalon fiber tow moving in a temperature gradient
($T_1 \le 1100°C$; $T_2 = 1150°C$; $T_3 = 1250°C$) at medium residence time
(v = 2.5 m/h) (adapted from ref. [42]).

Generally speaking, the FM-bonding is relatively weak, owing to the occurrence of additional thin layers of silica or/and carbon at the fiber/BN-coating or/and at the SiC-matrix/BN-coating interfaces [44-47, 51, 52]. Matrix crack deflection occurs at these weak interfaces (mostly at the former) and not within the BN-interphase. Carbon is also present as single layer in composites fabricated with pre-treated fibers (Nicalon and Hi-Nicalon) or stoichiometric fibers. It can be chemically removed before BN-deposition. S. Le Gallet et al. have reported that such a treatment increased the interfacial shear stress, without achieving the high values required for crack deflection within the interphase [52]. Finally, crack deflection according to these different scenarios can be modeled, as already discussed for the composites with PyC-interphases (see Fig. 2) [33, 34].

3.2.3- BN-interphases as deposited by CVI from organometallics

Another way to reduce corrosion during BN-deposition is through the use of halogen-free organometallic precursors [53]. S. Jacques et al. have deposited BN-interphases from tris(dimethylamino) borane, B $[N(CH_3)_2]_3$ in H_2-NH_3 flow, on Hi-Nicalon fibers (NH_3 being used to avoid the occurrence of free carbon in the coating). The tensile curves of their minicomposites is characteristic of SiC/SiC with relatively strong FM-bonding, high matrix crack density at failure and high interfacial shear stress (here, τ = 230 MPa). The latter is, to our knowledge, the highest value reported for SiC/BN/SiC composites. Finally, crack deflection did occur within the BN-interphase (Fig. 4), in accordance with the requirement of our layered interphase concept.

3.2.4- BN-interphases deposited on SiC fibers with in-situ generated BN-surface

The preceeding sections suggest that SiC-fibers with a carbon surface may not be the most appropriate for BN-deposition. An alternative would be to use SiC-fibers with a BN-surface. This can be achieved if a BN-film is formed at the expense of the fiber by radial diffusion coupled with reaction with an N-containing atmosphere [54-56].

A straightforward approach is to start with a stoichiometric SiC-fiber containing some boron (acting primarily as sintering aid) [26], as shown by M.D. Sacks and J.J. Brennan [54]. When such a fiber is treated at high temperature in an N-containing atmosphere, B-atoms diffuse radially from fiber core to react with nitrogen, yielding a strongly adherent BN-layer at fiber surface (typically, 100-200 nm thick). Further, diffusion in BN being anisotropic, the BN-coating grows with BN-layers

perpendicular to fiber surface and hence strongly bonded to the fiber. If now a BN-interphase is deposited on such a substrate by CVI, the BN-layers would have a tendency to be oriented, after some transition regime, parallel to the fiber surface [25, 27]. The so-called Sylramic-iBN and Super Sylramic-iBN fibers may have been developed on the basis of some related mechanism [55]. In the composites, crack deflection would occur either within the BN-interphase or at the BN-SiCm interface ("outside debonding"). These features could explain the good mechanical properties of these composites at high temperatures in oxidizing environment [43, 55, 57].
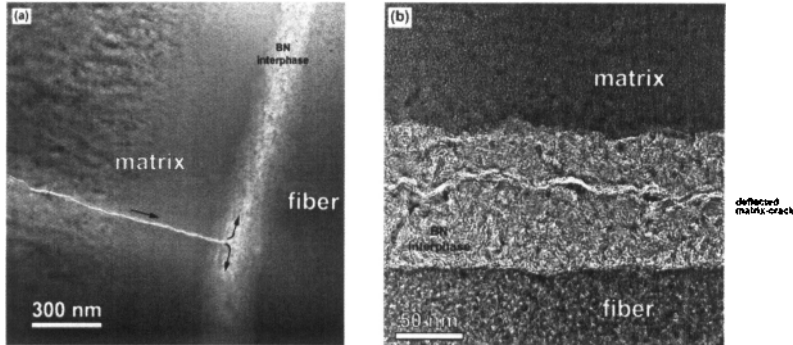

Fig. 4: 1D-SiC(HN)/BN/SiC(CVI) minicomposite with BN-interphase deposited from tris(dimethylamino)borane: matrix crack deflected within the BN-interphase, as seen by TEM (BF mode) at low (a) and high (b) magnifications (adapted from ref. [53]).

3.3- Multilayered $(X-Y)_n$ interphases

Multilayered (ML) interphases, $(X-Y)_n$, extend the concept of layered interphase to the nanometer scale, the interphase being now a stack of films of different materials X and Y, and the X-Y elementary sequence repeated n times. Their main advantage is that they can be highly tailored [1, 4, 5, 58]. As an example, the oxidation resistance of SiC/SiC could be improved by replacing PyC or BN interphases (100-200 nm thick) by $(PyC-SiC)_n$ or $(BN-SiC)_n$ ML-interphases in which the thickness of the oxidation-prone PyC or BN mechanical fuse is reduced to a few nanometers. This design criterion is based on oxygen gas phase diffusion consideration [35] and formation of healing condensed oxides (silica or/and boria) [13]. ML-interphases are deposited by CVI (switching from X to Y gaseous precursors) [58]. A key requirement is again a strong bonding between fiber surface and interphase.

3.3.1- $(PyC-SiC)_n$ multilayered interphases

Since the pioneering work of C. Droillard et al. [1, 2], $((PyC-SiC)_n$ ML-interphases have been used in a variety of SiC/SiC [59-65]. Depending on CVI-conditions, SiC-sublayers are either microcrystallized (with rough SiC/PyC interfaces) or nanocrystallized with smooth SiC/PyC interfaces. Sublayer thickness is ranging from 3 to 100 nm for PyC and 10 to 500 nm for SiC while the number of PyC-SiC sequences is in the range of 3 to 10. The first material deposited on fiber surface is usually PyC but it could also be SiC in an attempt to strengthen the fiber/interphase bonding [64, 65]. Both MLs with constant sublayer thickness or graded sublayer thickness (on PyC or/and SiC) have been used [1, 65].

Replacing a PyC single interphase by a $(PyC-SiC)_n$ ML-interphase *does not change markedly* their tensile properties, as shown for composites fabricated with Nicalon fibers (Fig. 1) [1]. Tensile curves fall into two groups depending on whether the fibers are pretreated (strong FM-bonding) or not

(weak FM-bonding). Similar conclusion can be drawn for SiC/SiC with Hi-Nicalon fibers [59, 60] or Tyranno SA stoichiometric fibers [65]. Crack deflection occurs at the fiber/interphase (or/and interphase/matrix) interface when the FM-bonding is weak (e.g. for as-received Nicalon or Hi-Nicalon fibers) and within the ML-interphase when it is strong enough (treated fibers). In this latter case, a matrix microcrack exhibits a dual propagation mode across the ML-interphase (Fig. 5) with an overall propagation path significantly lengthened [59, 60].

The lifetime of SiC/SiC with ML-interphase under load, at high temperature in air is improved with respect to their counterparts with single PyC-interphase [60, 66]. As an example, it increases from 2 to 48 hours for 2D-SiC (treated Nicalon)/SiC (CVI) composites, in tensile fatigue ($\sigma_{ap.}$ = 100 MPa) at 850°C, when a single PyC-interphase (50 nm thick) is replaced by a graded (PyC-SiC)$_4$ ML-interphase with e(PyC) = 50 nm and e(SiC) increasing from 50 to 150 nm when moving apart from fiber surface [66].

3.3.2- Other (X-Y)$_n$ multilayered interphases

At least two other ML-interphases, (BN-SiC)$_n$ and (PyC-TiC)$_n$, have been studied also with a view to improve the oxidation resistance. The potential advantage of the former lies in the fact that B-atoms are now present in the interphase, which favors crack-healing at intermediate temperatures. Unfortunately, experiments with pretreated Hi-Nicalon fibers have shown that the fiber/BN$_1$ bond is relatively weak, crack deflection occurring at that interface and not within the ML-interphase. Nevertheless, the lifetime in air at 700°C under load of minicomposites fabricated with Hi-Nicalon and a (BN$_{40}$-SiC$_{25}$)$_{10}$ ML interphase was significantly improved [9].

(PyC-TiC)$_n$ ML-interphases can also improve the oxidation resistance of SiC/SiC, although titanium oxides are not commonly regarded as healing oxides. Such interphases have been deposited on as-received Hi-Nicalon, according to a combination of conventional P-CVI (for PyC) and reactive P-CVI (for TiC) [67]. When the amount of TiC is low, each sublayer consists of a PyC-film reinforced with nanometric TiC-particles, which results in a strong FM-bonding. The lifetime of such minicomposites, under load in air at 700°C, is much higher (> 300 hours) than that (20 hours) for their counterparts with PyC single layer interphase. One of the reasons which could explain such unexpected behavior might be a strong interfacial bonding.
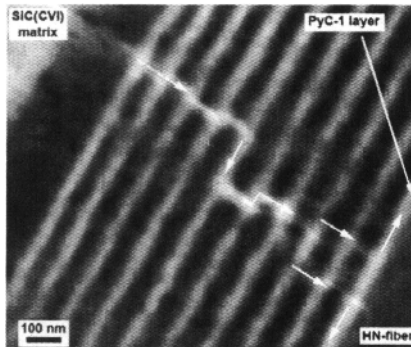

Fig. 5: 1D-SiC(HN)/SiC(CVI) with (PyC-SiC)$_{10}$ ML-interphase: TEM-image of a matrix microcrack deflected within the ML-interphase (adapted from ref. [60]).

3.4- Miscellaneous interphase materials

A few additional materials have been identified as potential interphase materials for SiC/SiC but with limited success up to now. This is the case for the ternary carbides (MAX-phases), such as Ti_3SiC_2 or Ti_3AlC_2, which display layered crystal structures. However, their deposition by CVD/CVI is difficult [68]. Further, they tend to grow with the layers perpendicular to the substrate surface and their ability to arrest/deflect a matrix crack in a CMC has not been formally established [69].

Oxides with layered crystal structures have been used as interphases in CMCs. This is the case for phyllosilicates (and related phyllosiloxides), such as mica fluorphlogopite KMg_3 $(AlSi_3)O_{10}F_2$ and the related phyllosiloxide $K(Mg_2Al)Si_4O_{12}$ [70]. However, their deposition (by sol gel process) is difficult, their thermal stability limited and their compatibility with SiC and SiC-CVI can be questioned. Other refractory oxides, such as zirconia, have also been considered but they do not have a layered crystal structure and hence, do not fall in our layered interphase concept [71].

Finally, porous interphases (also referred to as "pseudo-porous") consist of a mixture, at the nanometer scale, of a refractory material, such as SiC, with (fugitive) carbon [72]. However, such interphases do not display a marked anisotropic texture nor protect the fibers in an oxidizing environment and may undergo some sintering when exposed for a long time at high temperature.

4-   INTERPHASES IN SiC/SiC FOR HT-NUCLEAR REACTORS

SiC/SiC are potential structural materials for both fission and fusion high temperature nuclear reactors [15-17, 73]. This new and extremely demanding application raises specific constraints on the fibers, the matrix and the interphases.

4.1- SiC/SiC environment in HT nuclear reactors

The environment that would see SiC/SiC in e.g. gas cooled fast reactors is not so different from that they presently experience in advanced gas turbines, in terms of temperature, gas pressure and lifetime. However, they are not expected to see permanently oxidizing atmospheres. More importantly, they would be continuously exposed to intense irradiation by fast neutrons, α-particles and electromagnetic radiations. In high temperature advanced fission reactors, SiC/SiC will be exposed to moderately energetic neutrons (≈ 2 MeV) but at temperatures that could be higher than about 1200°C, whereas in Tokamak fusion reactor blankets, they will be irradiated by much more energetic neutrons (14.1 MeV) formed during the deuterium/tritrium fusion reaction but likely at somewhat lower temperatures.

Such severe irradiation conditions are known to change (in a more or less dramatic manner) the structure of materials and hence their properties, as briefly discussed in the following sections for the SiC/SiC and their constituents, on the basis of literature data.

4.1.1- Irradiation of silicon carbide

Monolithic SiC undergoes a moderate swelling when irradiated by neutrons, as the result of amorphization or point defect formation at low temperature and cavity formation at high temperature. It first decreases as temperature is raised, passes through a minimum (0.2 to 0.4 vol% for a dose of 1-8 dpa) at 1100-1200°C, then increases to reach 1.5 vol% at 1600°C [17, 73]. SiC-matrix when deposited by CVI is pure, well crystallized and assumed to behave as monolithic SiC.

The effect of neutron irradiation on SiC-based fibers strongly depends on their composition and structure. On the one hand, stoichiometric fibers, which are well crystallized and with a small impurity content, also behave like monolithic SiC. On the other hand, Si-C-O (Nicalon-type) and SiC+C (Hi-Nicalon) fibers, prepared at lower temperature and poorly crystallized, undergo a permanent shrinkage [74].

As a result of this volume change mismatch upon neutron irradiation between SiC (CVI) matrix and $1^{st}/2^{nd}$ SiC fiber generations, debonding at FM-interface usually occurs with mechanical degradation [73, 75]. This key feature explains why stoichiometric SiC fibers are preferred for SiC/SiC to be used in nuclear reactors.

4.1.2- Neutron irradiation of interphase materials

Boron nitride, as an interphase, is poorly compatible with nuclear reactor environment [76, 77]. Firstly, $^{10}_{5}B$ isotope (present at a level of $\approx$ 20 at.% in natural boron) has an extremely high neutron capture cross section. Hence, the use of BN-interphase would suppose that it is deposited from $^{11}_{5}B$-enriched gaseous precursor. Secondly, boron nitride when neutron irradiated, undergoes nuclear reactions producing gaseous species (helium) and radioactive long life species (such as $^{14}_{6}C$). Further, since in a nuclear reactor the atmosphere is, in principle, not oxidizing, BN-interphases are, for all these reasons, not used in this field of application.

PyC-based interphases have been up to now the interphases of choice. However, they raise a problem of anisotropic dimensional change under neutron irradiation strongly depending on their degree of crystallization. Graphite and HOPG undergo a moderate shrinkage along the a-axis, i.e. parallel to graphene layer, and a swelling along the perpendicular c-axis. This anisotropy is strong at low temperature/high irradiation dose but it decreases as irradiation temperature is raised [78]. The behavior of turbostratic pyrocarbon is more complex. Although similar to that of graphite parallel to graphene layers, it first shrinks in a perpendicular direction at low irradiation dose and then swells [21, 79]. Since in a PyC-interphase graphene layers are preferably oriented parallel to the fiber surface, this dimensional change anisotropy may modify residual thermal stresses (particularly in radial direction) and alter the FM-bonding. Hence, the interphase may be again the vulnerable constituent of SiC/SiC when exposed in a prolonged manner to neutron irradiation. Potential solutions to overcome this difficulty are those already discussed in section 3, [16, 17, 80].

Finally, pseudo-porous SiC-interphases might also be an alternative as previously mentioned [16, 72, 80]. However, their dimensional stability under neutron irradiation is not well known. It may shrink (if it does contain enough free carbon), changing the residual stress field and favoring debonding.

4.2- Irradiated SiC/SiC

A compilation of flexural strength data reported by different authors, for a variety of SiC/PyC/SiC composites which have been neutron irradiated (in a broad temperature range: 200-1000°C) suggests that: (i) there is no loss in strength up to an irradiation dose of 10 dpa for materials fabricated with stoichiometric SiC-fibers, but conversely, (ii) the strength drops by $\approx$ 60% almost linearly when irradiation dose increases up to 10 dpa for those with Si-C-O (Nicalon) or SiC + C (Hi-Nicalon) fibers [16, 73, 81]. This result is consistent with the dimensional change (permanent shrinkage) reported for these two latter fibers, which lowers the FM-bonding and load transfer. However, it would be more appropriate to rely on data determined using tensile tests. Hence, the analysis of the effects of neutron irradiation and interphase design on the mechanical properties of SiC/SiC should be pursued for composites with stoichiometric fibers, using tensile tests and analysis of microstructure-strength relations using appropriate models.

Fig. 6 shows tensile curve for SiC (HN-S)/PyC/SiC(CVI) composites recorded at ambient after neutron irradiation at 1000°C [19-21, 82]. For such a composite with a thick-PyC single layer interphase, the features of the tensile curve after irradiation show a weakening of the FM-bonding (with a plateau-like shape, broad hysteresis loops, and some residual strain after unloading). Further, the strain to failure is high (and close to that of dry tow under tension) as opposed to that of the

unirradiated material (which seems to exhibit a premature failure) [82]. Irradiation at higher dose (up to ≈ 8 dpa at 800°C) of composites with still thicker PyC-interphase (≈ 700 nm) did not change markedly the tensile behavior after irradiation [20]. Since the thickness of the PyC-interphase is here extremely large (vs 100-200 nm in most SiC/SiC), the change in tensile behavior could be tentatively attributed to an evolution of the PyC-nanotexture during irradiation.

2D-SiC (HN-S)/PyC/SiC (CVI) composites, with much thinner PyC interphase (50-60 nm), display after neutron irradiation (750°C with dose up to 12 dpa), a very different behavior [19]. Their tensile curves (not shown in Fig. 6), before and after irradiation are very similar, with convex curvature up to failure, relatively narrow hysteresis loops and limited residual strain after unloading. These features suggest a relatively strong FM-bonding and little evolution of the interfacial zone during irradiation. However, in both cases, the strain-to-failure is low comparatively to that of the fiber. Hence, reducing the thickness of the PyC-interphase in composites fabricated with Hi-Nicalon S fibers, seems to enhance the stability of the FM-interphase bonding. It is noteworthy that such a conclusion cannot be drawn for those produced from Tyranno SA (where the FM-bonding seems to be higher and not to markedly depend on PyC-thickness) [17].
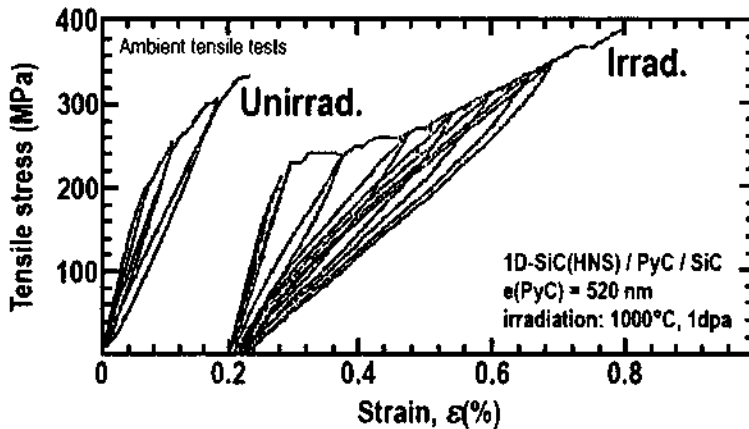

Fig. 6: Tensile curves of SiC/PyC/SiC composites with Hi-Nicalon type S SiC fibers and thick PyC interphase, before and after neutron irradiation, (adapted from ref. [82]).

Replacing the PyC single layer interphase by a (PyC-SiC)$_n$ ML-interphase (with (e(PyC) = 20 nm, e(SiC) = 100 nm and n = 5) yields relatively brittle composites, with extremely limited non-linear domain and very low strain at failure (≈ 0.1%). Their tensile curves after neutron irradiation (≈ 8 dpa ; 800°C) are similar to those of their un-irradiated counterparts [20]. Finally, composites with "pseudoporous" SiC interphases have also been irradiated and mechanically tested [16, 83].

5- CONCLUDING REMARKS
1- The interphases in SiC/SiC are ideally materials with a layered structure, in which the layers are parallel to the fiber surface, weakly bonded to one another but strongly adherent to the fiber. Matrix crack deflection occurs within the interphase in a diffuse manner and over short distances.

2- Anisotropic pyrocarbon is the interphase of   choice. It is deposited by CVI with graphene layers parallel to fiber surface. Achieving a strong bonding between the interphase and the fiber is not straightforward, and it may require a fiber pretreatment. The optimal PyC-thickness depends on both residual thermal stresses and fiber roughness. SiC/SiC with optimized PyC-interphase displays high load transfer and good mechanical properties under static or cyclic loadings in a broad temperature range. Unfortunately, pyrocarbon is oxidation-prone even at low temperatures.

3- BN layered interphase is more resistant to oxidation. However, its deposition by CVI with optimal structure and bonding to the fiber, is not straightforward. BF_3-NH_3 is a corrosive precursor whereas $BCl_3-NH_3-H_2$ requires high temperature to achieve high crystallinity and corrosion resistance. Corrosion problem could be solved through the use of TG-CVI or halogen-free organometallic precursor. Finally, achieving a strong fiber/BN-bonding remains a key issue. One way to solve this difficulty might be to use pretreated (stoichiometric) fibers with a BN-surface.

4- Another way to improve oxidation resistance of SiC/SiC is to reduce the thickness of PyC-interphase and to play with self-healing phenomena. SiC/SiC with $(X-Y)_n$ interphases (with X = PyC or BN and Y = SiC or TiC) displays improved lifetime under load in oxidizing atmospheres. The concept of multilayered material associated with self-healing phenomena, is still more efficient when extended to the matrix itself, oxygen being entrapped far from the fiber surface and interphase, with unmatched composite lifetimes.

5- The use of SiC/SiC in high temperature nuclear reactors is a relatively new field of application. BN being excluded from nuclear consideration, the best interphase material seems again to be pyrocarbon. However, pyrocarbon is not dimensionally stable under fast neutron irradiation, which may alter FM-bonding and composite mechanical properties. An approach to solve this problem is to lower the volume fraction of pyrocarbon in the interphase by either reducing its thickness (single or ML-interphases) to few nanometers or replacing pure carbon by C-SiC mixtures at the nanometer scale. Preliminary data suggest that the mechanical behavior of SiC/SiC with such interphases is not significantly degraded after neutron irradiation at 700-1000°C up to $\approx$ 10 dpa. However, more studies, including both representative mechanical testing and structure analysis of the interfacial zone (HR-TEM) should be pursued before considering that SiC/SiC fully meet all the requirements of this new and demanding application.

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