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Boron-bearing species in ceramic matrix composites for long-term aerospace applications

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Abstract

Boron-bearing refractory species are introduced in non-oxide ceramic matrix fibrous composites (such as SiC/SiC composites) to improve their oxidation resistance under load at high temperatures with a view to applications in the aerospace field. B-doped pyrocarbon and hex-BN have been successfully used as interphase (instead of pure pyrocarbon) either as homogeneous or multilayered fiber coatings, to arrest and deflect matrix cracks formed under load (mechanical fuse function) and to give toughness to the materials. A self-healing multilayered matrix is designed and used in a model composite, which combines B-doped pyrocarbon mechanical fuse layers and B- and Si-bearing compound (namely B_4C and SiC) layers forming B_2O_3-based fluid healing phases when exposed to an oxidizing atmosphere. All the materials are deposited by chemical vapor infiltration. Lifetimes under tensile loading of several hundreds hours at high temperatures are reported.

Keywords: Ceramic matrix composites (CMC); C(B) and BN interphases; B_4C/SiC multilayered matrices; B_2O_3-healing phase; CVD-processing

1. Introduction

Ceramic matrix composites (CMCs) consist of ceramic fibers embedded in a ceramic matrix. The most commonly used CMCs are those comprising carbon or SiC-based fibers (arranged in a multidirectional architecture) in a carbon or SiC matrix deposited according to a gas or liquid phase route. C/C, C/SiC and SiC/SiC composites (the fibers being quoted first) are potential candidates for a variety of applications in the aerospace field including rocket nozzles, aeronautic jet engines, heat shields and aircraft braking systems. CMCs are *non-brittle* materials when the fiber/matrix (FM) bonding has been properly optimized during processing, i.e. when the FM-bonding is not too strong nor too weak [1–3]. The FM-bonding is controlled through the use of an *interphase*, which is a thin film of a material with a low shear strength, deposited on the fiber surface prior to the infiltration of the matrix in the fiber architecture (or fiber preform). In terms of mechanical behavior under load, CMCs are referred to as *inverse* composites, which is to say that the matrix failure strain is lower than that of the fibers, hence, under increasing load, it is the matrix which fails first. All the constituents being brittle, one has to avoid the early failure of the fibers by notch effect when matrix undergoes microcracking (at low strain). To achieve this key requirement, the FM-interface (or the interphase) should arrest or/and deflect the matrix microcracks thus acting as a mechanical fuse (to protect the fibers). Under such conditions, CMCs display a non-linear stress/strain behavior related to various damaging phenomena at the microscopic scale (matrix cracking, FM-debonding and FM-friction) and a high fracture energy. In terms of interphase design, it has been postulated that the best interphase materials might be those with a layered crystal structure (such as anisotropic pyrocarbon) or microstructure (such as $(\text{PyC–SiC})_n$ multilayers), the layers being relatively weakly bonded to one another, deposited parallel to the fiber surface, and strongly bonded to the fiber [4–7]. Consequently and for the applications mentioned previously, C/PyC/SiC or SiC/PyC/SiC (the pyrocarbon interphase being quoted between the fiber and the matrix) might be the best materials in terms of mechanical functions; however, both carbon and SiC are intrinsically oxidation-prone.

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For long-term applications in engines, non-oxide CMCs have to be highly engineered in order to improve their oxidation resistance, particularly at the level of the interphase and of the matrix. In this field, *boron-bearing species* appear to be promising. Firstly, anisotropic pyrocarbon interphase could be replaced either by boron-doped pyrocarbon or hexagonal boron nitride, all of them displaying layered crystal structures with weak interlayer bonding as well as an enhanced oxidation resistance [8–13]. Secondly, an important property of all B-bearing species is to form fluid oxide phases (B_2O_3 or B–*M*–O ternary phase) over a broad temperature range (600–1200°C for B_2O_3) when heated in an oxidizing atmosphere. These B-bearing species, if introduced in the interphase or matrix of non-oxide CMCs, could be used to design *self-healing* materials (the fluid oxide phase formed in situ by oxidation, filling matrix cracks, slowing down the in-depth diffusion of oxygen) with improved lifetimes [14, 15].

The aim of the present contribution is to give an overview of the research work, performed at LCTS and elsewhere, on the improvement of the oxidation resistance and lifetime under load in oxidizing atmospheres of non-oxide CMCs, through the use of B-bearing species (such as B-doped carbon, hex-BN and boron carbides) in the interphase or/and matrix of non-oxide CMCs.

2. Experimental

2.1. Materials and processing

The starting materials used had the following purity: CH_3SiCl_3 (MTS): 97–99%; CH_4 (N35): 99.95%; C_3H_8 (N25): 99.5%; BCl_3 (N25): 99.5% and NH_3 (N36): 99.96% with $H_2O \leqslant 200$ ppm. All the CMCs considered here were produced by chemical vapor infiltration (CVI). In this process, a fiber architecture (which can be either a simple fiber tow or a multidirectional fiber preform) is chemically coated with a ceramic interphase (such as C(B) or BN) and then densified with a ceramic matrix (such as SiC or a multilayered SiC-based matrix containing boron-bearing species), in a hot wall deposition chamber, from appropriate gaseous precursors [16, 17]. Few experiments were also performed with flat substrates (such as small disks of graphite, SiC or silica) in order to assess deposition kinetic laws and mechanisms. As an example, Fig. 1 shows the apparatus used to study the kinetics of deposition of BN from BF_3–NH_3 gas mixtures [10].

A variety of gaseous precursors can be used to deposit the ceramics which are of interest here (pyrocarbon; C(B), SiC, BN, B_4C and Si–B–C). Some of the most classical precursors and related overall deposition reactions in the field of CMC-CVI processing are:

$$2C_xH_y \rightarrow 2xC + yH_2, \tag{1}$$

$$CH_3SiCl_3 \xrightarrow{H_2} SiC + 3HCl, \tag{2}$$

$$BX_3 + NH_3 \rightarrow BN + 3HX \quad \text{with } X = F, Cl, \tag{3}$$

$$4BCl_3 + CH_4 + 4H_2 \rightarrow B_4C + 12HCl. \tag{4}$$

As a matter of fact the actual deposition chemical mechanisms are much more complex and depend on deposition conditions (temperature *T*, pressure *P*, gas flow rate *Q*, precursor composition). They usually involve chemical reactions occurring in the gas phase (homogeneous reactions) and leading to the formation of intermediate gaseous species as well as chemical reactions taking place at the substrate surface (heterogeneous reactions). Deposition is rate-controlled either by the mass transfers of gaseous species through the boundary layer (MTR: mass transfer regime) or by the kinetics of the chemical reactions, particularly those

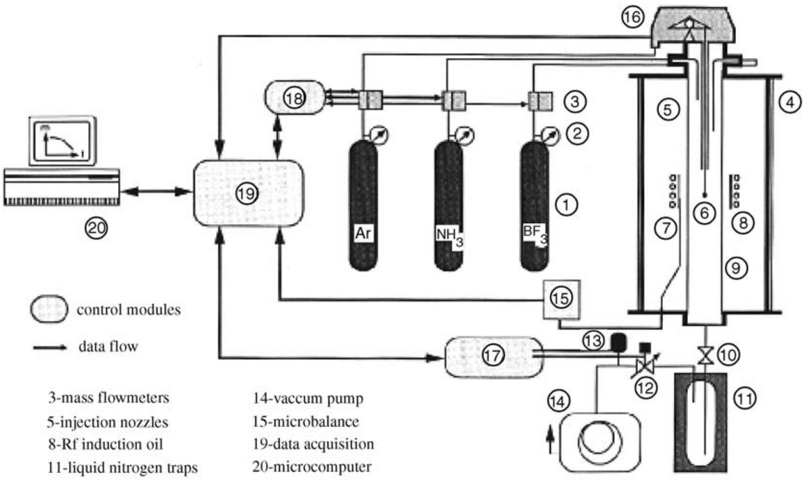

Fig. 1. Apparatus used to study the kinetics of deposition of BN on a flat substrate (6) from BF_3–NH_3–Ar gaseous mixtures [10].

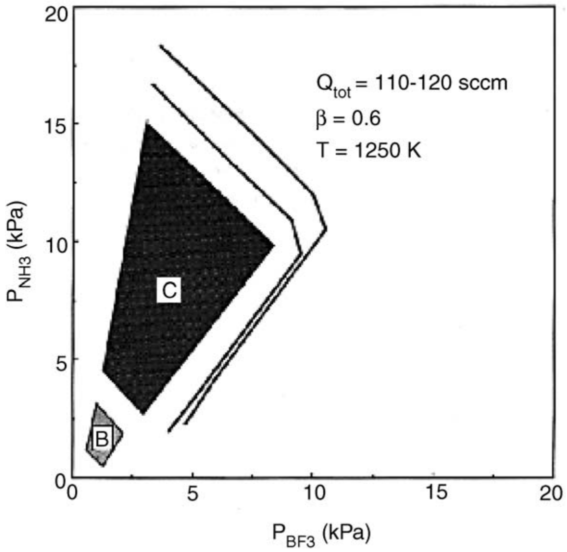

Fig. 2. Kinetic domains for the deposition of BN from BF_3–NH_3–Ar. Subdomains B and C correspond to kinetic laws (5) and (6). Composition of the precursor is defined with $\alpha = P_{NH_3}/ P_{NH_3} + P_{BF_3}$ and $\beta = P_{Ar}/(P_{BF_3} + P_{NH_3})$ [11].

occurring at the substrate surface (CRR: chemical reaction regime). The knowledge of the *P–T–Q* domains in which the deposition of given ceramics is rate-controlled by mass transfers or reaction kinetics is important since the densification of a porous fiber preform is more homogeneous when it is performed under CRR-conditions, i.e. usually at low *T*, *P* where the reaction kinetics are slow with respect to the diffusion of the gaseous species in the pore network [16, 17]. As an example, Fig. 2 shows the kinetic diagram, established experimentally with the apparatus shown in Fig. 1, for the deposition of BN from $BF_3 - NH_3 - Ar$, at a relatively low temperature ($T = 1250\,K$) compatible with the infiltration of BN in a porous body [11]. At this temperature, a transition zone is observed between a mass transfer regime and chemical reaction regimes. Within the CRR-domain, deposition of BN occurs according to two different kinetic laws and mechanisms corresponding to different apparent activation energies and reactions orders, namely:

Subdomain B:

$$R = k_o \exp\,(-E_a/RT)P^{0}_{BF_3}P^{0}_{NH_3}, P^{-1}_{HF} \quad \text{with } E_a = 100\ \text{kJ/mol.} \tag{5}$$

Subdomain C:

$$R = k_o \exp\,(-E_a/RT)P^{1.5}_{BF_3}P^{0}_{NH_3}, P^{-2}_{HF} \quad \text{with } E_a = 185\ \text{kJ/mol.} \tag{6}$$

The densification of a fiber preform by CVI yields composites with a high quality matrix, in terms of microstructure and mechanical properties, but with some residual open porosity (typically 10–15%), which favors the in-depth diffusion of oxygen towards the interphase and the fibers when the materials are used under load in oxidizing atmospheres.

2.2. Characterization

The structure and microstructure of the FM-interfacial zone (whose thickness is lower than 1 μm) and of the matrix (which is complex when consisting of a multilayered ceramic) have been characterized by electron microscopy. The mechanical behavior was assessed through tensile tests performed on model (one-dimensional (1D) fiber architecture) or real (*n*D fiber architecture) composites. The oxidation of the composites was studied through thermogravimetric analysis (TGA) experiments performed in dry air. Finally, the durability of the composites was characterized through static fatigue tests (constant applied load) in air at different temperatures.

3. Interphase design with boron-bearing species

The objective here is to replace the pyrocarbon interphase, by a boron-containing material displaying a layered crystal structure or microstructure, to act as a mechanical fuse (matrix crack deflection), as well as a better oxidation resistance (related to the formation of a B_2O_3-condensed phase when considering an oxidizing atmosphere). Three different interphases have been considered, namely boron-doped pyrocarbon, C(B), hexagonal boron nitride, BN, and $(BN–SiC)_n$ multilayers. For all these materials, the oxidation resistance improvement is related to the formation of a B_2O_3 or B_2O_3–SiO_2 fluid phase resulting from the oxidation of the boron and silicon-bearing species, according to the following overall equations:

$$2B_{(s)} + 3/2O_{2(g)} \rightarrow B_2O_{3(l)}, \tag{7}$$

$$2BN_{(s)} + 3/2O_{2(g)} \rightarrow B_2O_{3(l)} + N_{2(g)}, \tag{8}$$

$$SiC_{(s)} + 2O_{2(g)} \rightarrow SiO_{2(s,l)} + CO_{(g)}, \tag{9}$$

$$SiC_{(s)} + 3/2O_{2(g)} \rightarrow SiO_{2(s,l)} + CO_{(g)}. \tag{9'}$$

B_2O_3 has a low "melting point" (≈450°C) and its viscosity decreases as temperature is raised. It remains in the liquid state up to a temperature of about 1100°C in a dry atmosphere but it is readily gasified at low temperatures if the atmosphere contains moisture. Finally, the viscosity and thermal stability of the fluid oxide phase can be tailored if the oxide phase contains both B_2O_3 and SiO_2.

3.1. Boron-doped pyrocarbon C(B) interphases

C(B) CVD-deposits of various compositions have been deposited on flat substrates or Si–C–O (Nicalon) fibers from a gaseous precursor containing simultaneously a boron-bearing species (i.e. a boron halide), a carbon-bearing species (i.e. a hydrocarbon) and a gas carrier [18]. The boron content ranges from 0 (pure pyrocarbon) to 33 at%. The addition of boron first increases the anisotropy of the pyrocarbon deposit (specimen II), as supported by optical microscopy (OM), X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM) data (Table 1). Then, the anisotropy decreases as the B-content of the deposit increases, deposits IV (20 at% B) and V (33 at% B) being almost isotropic. Hence, the C(B) deposit with the lowest B-content (specimen II) displays a layered structure similar to (and even better than) that of the undoped pyrocarbon, compatible with the mechanical fuse function of an interphase [5–7].

Table 1
Structural parameters of C(B) deposits with increasing boron content

	Specimen				
	I	II	III	IV	V
B-content (at%)[a]	0	8.3	15.1	20.0	33
A_e(°)[b]	10	19	11	ND	ND
O_A(°)[c]	94	72	107	ND	ND
d_{002} (pm)[d]	346	339	337	341	≈367
L_c(nm)[d]	5.3	10.7	8.5	≈1.7	≈1
N[e]	6	11	9	4	3
L_1 (nm)[e]	0.4	1	0.6	0.3	0.2
L_2 (nm)[e]	2.8	5	2.3	1.5	0.9

[a] Electron probe microanalysis (EPMA).
[b] Extinction angle measured by OM in polarized light.
[c] Orientation angle measured on 002 arc (TEM-SAD pattern).
[d] From XRD-pattern.
[e] From HR-TEM images (*N*: number of fringes in a stack, L1 and L2 size of the fringes) [18].

Oxidation TGA experiments performed in dry flowing air at 700°C, show that the overall weight loss rate (resulting from the competition between the oxidation of carbon producing gaseous carbon oxides with a weight loss and that of boron giving condensed B_2O_3 with a weight gain) continuously decreases as the B-content of the deposit increases, to become very low for specimen V. Hence, C(B) deposits display two contradictory properties in terms of interphase requirements: the highest anisotropy (fuse function) is observed for the lowest B-content (specimen II) whereas the best oxidation resistance is achieved with the highest one (specimen V) [18].

To take into account these two contradictory features, multilayered C(B) deposits were designed and deposited on single Si–C–O (Nicalon) fiber to produce after the deposition of SiC-matrix, so-called model microcomposites, as shown in Fig. 3a. In this complex interphase, each layer has a thickness of 100 nm. The first layer (I) deposited on the fiber surface consists of pure pyrocarbon (to achieve a good bonding with the fiber) whereas the following layers (II—IV in interphase A and II—V in interphase A′) display increasing B-content. As expected from the layered interphase concept [4–7], cracks formed in the brittle SiC-matrix under tensile loading were deflected near the layers with the highest anisotropy (layer 2) (Fig. 3b). Further, static fatigue tests performed in air at 600°C under constant tensile loading (the stress level being close to the proportional limit to create open cracks in the matrix), showed that the lifetime of these model microcomposites is increased when compared to that of their counterpart with a single pyrocarbon (type I) interphase (Fig. 4). The lifetime increase is related to a self-healing behavior of the composites when they are exposed to an oxidizing atmosphere at a sufficient temperature. Oxygen diffusing along the matrix cracks reacts first with the boron-rich C(B) layers (layers V to III) giving a fluid oxide phase (mainly B_2O_3) which fills the cracks, slows down the in-depth diffusion of oxygen towards the B-poor

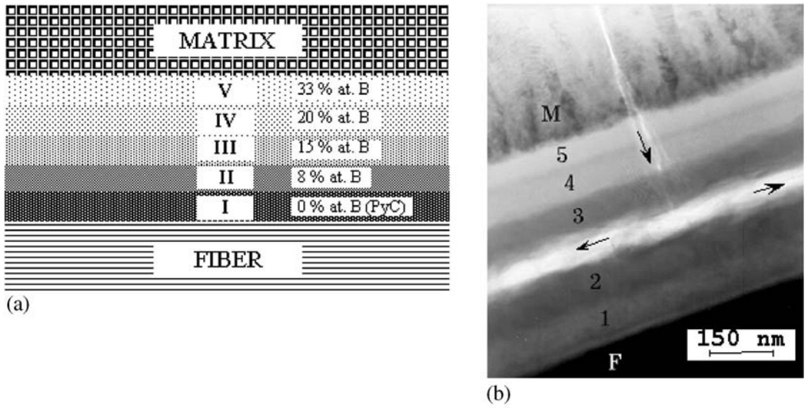

Fig. 3. Multilayered C(B) interphase (type A′) in a 1D-Si–C–O (Nicalon)/SiC microcomposite: (a) composition of the interphase, (b) matrix crack deflection in the interphase near layer II [18].

inner layers (layers II and I) and prevents an early fiber failure.

3.2. Hexagonal boron nitride interphases

Hexagonal BN is another B-containing material (50 at%) of potential interest in the field of interphase for non-oxide CMCs. It has a layered structure very similar to that of pyrocarbon and a better oxidation resistance, as discussed previously. However, it is often poorly crystallized when deposited at low temperatures (CVI-conditions) and consequently it reacts with oxygen and moisture. Despite this drawback, BN-interphase has been used since a long time in SiC/SiC composites [4–13].

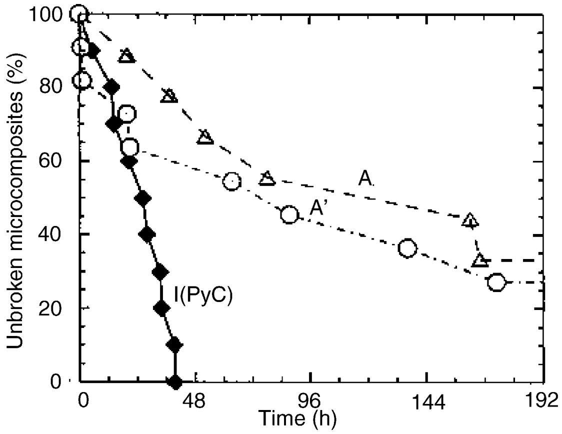

Fig. 4. Lifetime of Si–C–O (Nicalon)/SiC microcomposites, under static fatigue (constant tensile 800 MPa stress) in air at 600°C, with different FM interphases. I is a single layer pyrocarbon interphase, A′ is the five layers interphase shown in Fig. 3 and A a four layers interphase (layer V being missing) [18].

BN can be deposited from a variety of gaseous precursors including B_2H_6–NH_3 or $B_3N_3H_6$ and BX_3—NH3 (with X = F, Cl) [19]. The main advantage of B–N–H precursors lies in the fact that they yield BN deposits at low temperatures (250–650°C) and display a good compatibility with SiC-fibers. Conversely, the BN-deposits are amorphous or poorly crystallized. Finally, these precursors should be handled with care (B_2H_6) or are not readily available ($B_3N_3H_6$). Hence, the most commonly used BN-precursors are BX_3–NH_3 (with X = F, Cl) [8–13, 19–21]. The main advantage of BF_3–NH_3 lies in the fact that Eq. (3) can yield well-crystallized BN deposits (with the BN-layers parallel to the substrate surface) even under the low T–P conditions required by the CVI-process (Fig. 5). Further both the BN-yield corresponding to Eq. (3) and the deposition rate are low, which favor infiltration. Conversely, both BF_3 and HF are corrosive species for SiC fibers and the bonding between these well-crystallized BN deposits and SiC fibers is weak. One way to take into account these contradictory features is to design bi-layer interphases with: (i) a thin layer of BN deposited under low T–P conditions, poorly crystallized but adherent to the fiber and (ii) a second layer deposited under conditions yielding 3D-ordered BN (conditions 5 in Fig. 5) acting as a mechanical fuse (crack deflection) and exhibiting a good oxidation resistance [22].

BCl_3 and the HCl reaction product (Eq. (3)) are less corrosive with respect to SiC fibers than their fluorine-bearing counterparts. Further, the BN-deposition kinetics, under commonly used CVI-conditions, is faster and the BN-yield higher. Conversely, boron nitride deposited from BCl_3–NH_3 is often poorly crystallized and hence oxidation-prone and sensitive to moisture. The state of crystallization of BN deposits can be

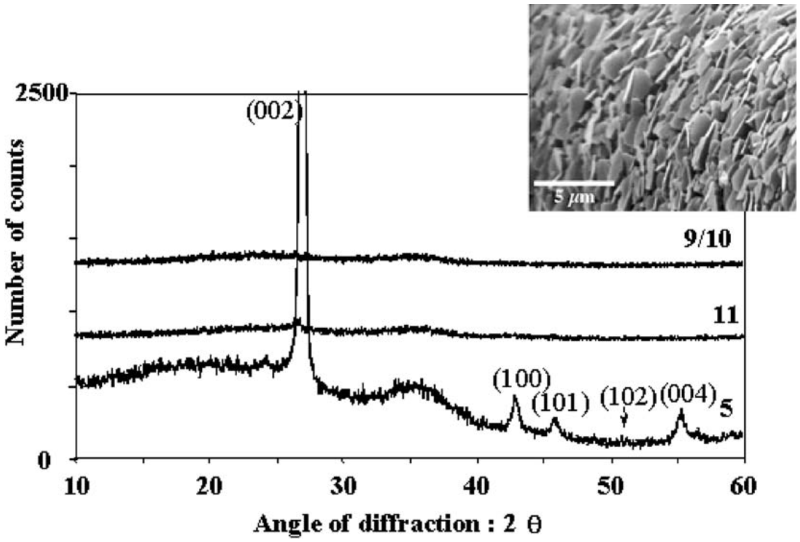

Fig. 5. Crystallinity of BN films deposited from BF_3–NH_3 under different T–P–α conditions: (a) XRD patterns of films deposited on Si–C–O Nicalon fibers, (b) SEM-image of film deposited under conditions 5 [22].

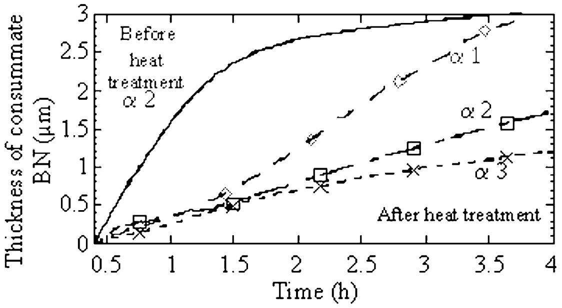

Fig. 6. Oxidation at 950°C in dry air of BN-films deposited from BCl_3–NH_3 showing the effect of the $\alpha = NH_3/BCl_3$ ratio (with $\alpha_3 > \alpha_2 > \alpha_1$) and of a post deposition annealing treatment [13].

improved when they are deposited with a NH_3-rich precursor ($\alpha = NH_3/BCl_3 > 1$) and when an annealing treatment, at the highest temperature compatible with the fiber thermal stability is applied to the coated fibers after BN-deposition. As a result, the oxidation resistance is also improved (Fig. 6) [19]. Finally, the oxidation resistance of boron nitride deposited from BCl_3–NH_3 has been reported to be improved when it has been doped with silicon [19, 23].

Static fatigue tests in air at 700°C, performed on model 1D-Si–C (Hi-Nicalon)/BN/SiC minicomposites (fiber tow architecture) have shown that the lifetime was better than that observed for their counterparts with a pyrocarbon interphase [19, 24].

3.3. $(BN–SiC)_n$ multilayered interphases

The concept of multilayered $(X–Y)_n$ interphase was introduced to enlarge the small family of materials with a layered crystal structure (PyC; BN) that could be used to optimize the FM coupling in CMCs, moving from the atomic scale (atomic planes weakly bonded to one another) to the nanometer scale (weakly bonded layers with an elementary thickness of a few nm or a few 10 nm) [4–7]. $(X–Y)_n$ multilayered interphases offer a number of advantages, e.g., their composition and microstructure can be tailored. As an example, *X* can be a phase with a layered crystal structure (such as PyC or BN) and *Y* a material forming a fluid oxide phase when exposed to an oxidizing atmosphere (such as SiC), resulting in $(PyC–SiC)_n$ or $(BN–SiC)_n$ multilayered interphases. Here, the parameters which can be adjusted are the thicknesses of the elementary layers *e*(PyC), *e*(BN) and *e*(SiC) as well as the number of elementary sequences, *n* (with typically *n* ranging from 4 to 30). Such multilayered interphases can be infiltrated in a porous body (e.g., a fiber preform) by pressure-pulsed CVI (P-CVI) utilizing in a sequenced manner different gaseous precursors [25].

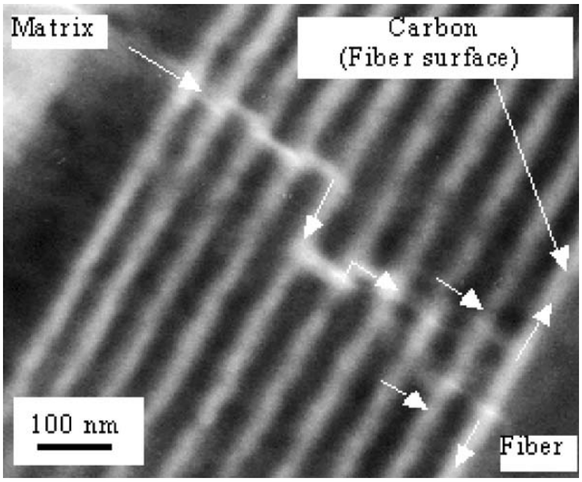

Fig. 7. Crack deflection under tensile loading in a SiC (Hi-Nicalon)/SiC minicomposite with a multilayered $(PyC_{20}–SiC_{50})_{10}$ interphase. The white layers are PyC layers and the black layers are SiC layers [26].

Multilayered interphases deflect matrix cracks in a complex manner, as shown in Fig. 7 for a Si–C (Hi-Nicalon)/$(PyC_{20}–SiC_{50})_{10}$/SiC model minicomposite (the figures showing the thickness of the elementary layers (in nm) and the number of elementary sequences, respectively). Oxygen diffusing along such cracks has to follow a complex path. During this diffusion, it reacts with BN or and SiC to form fluid phases, namely B_2O_3, SiO_2 or B_2O_3–SiO_2 liquid phases (depending on layer composition and temperature), that tend to fill the cracks (as soon as they are created and as long as they remain open) and to slow down the in-depth diffusion of oxygen towards the fibers (diffusion coefficients being much lower in condensed phases than in gas phases). As a result the lifetime of the composites is improved [25].

4. Matrix design with boron-bearing species

Boron-bearing species can also be introduced in the SiC-matrix itself to further improve the oxidation resistance of CMCs through the in-situ formation of fluid oxide phases based on B_2O_3. In addition to BN, previously discussed in Section 3, other boron compounds, such as boron carbide (formulated here as B_4C but which is known to display a relatively broad homogeneity domain) and boron silicides (SiB_x with $x = 3, 6, 14$) are potential candidates since they can be in equilibrium with SiC at high temperatures, as shown in Fig. 8 [27]. When dispersed in a SiC-matrix, e.g., as thin layers, these compounds form B_2O_3-based oxides by reacting with oxygen diffusing along matrix cracks, according to the following overall equations:

$$B_4C_{(s)} + 4O_2 \rightarrow 2B_2O_{3(l)} + CO_{2(g)}, \tag{10}$$

$$2SiB_{3(s)} + 13/2O_2 \rightarrow 2SiO_{2(s,l)} + 3B_2O_{3(l)}, \tag{11}$$

$$SiB_{6(s)} + 11/2O_2 \rightarrow SiO_{2(s,l)} + 3B_2O_{3(l)}, \tag{11'}$$

$$SiB_{14(s)} + 23/2O_2 \rightarrow SiO_{2(s,l)} + 7B_2O_{3(l)}. \tag{11''}$$

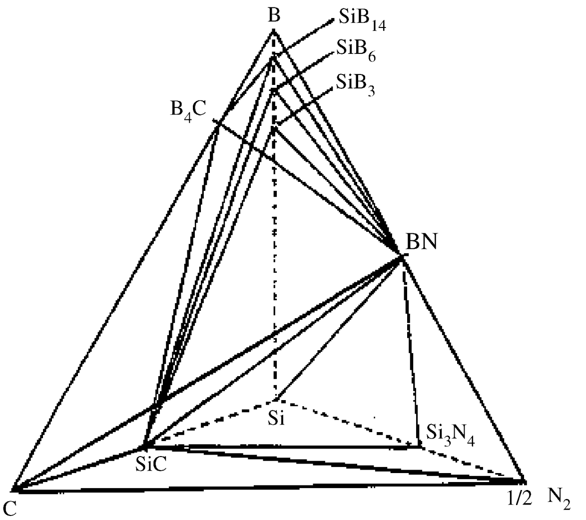

Fig. 8. Main features of the quaternary Si–B–C–N phase diagram, for $T = 1500\,\mathrm{K}$, as calculated by P. Metais and C. Bernard [27].

All these compounds are refractory and can be deposited from gaseous precursors. Further, since densification under CVI-conditions is performed at relatively low temperatures, these compounds are often amorphous (or nanocrystallized) which still increase the composition flexibility. Finally, as long as these phases only act as a source of boron (and not necessarily as mechanical fuse), layered crystal structures are not required.

Fig. 8 shows an example of a self-healing matrix which has been infiltrated within a fiber tow by P-CVI, utilizing a hydrocarbon as a C-source and a boron halide as a B-source [14]. The matrix is the repetition of an elementary sequence S comprising a mechanical fuse (a boron-doped pyrocarbon formulated here B_xC_y with $x \approx 0.1$), a B-source layer (a boron carbide, $B_{13}C_2$) and a Si-source (SiC). This sequence has been repeated four times, with different elementary thicknesses in order to increase the volume fraction of the B-bearing phase when moving a part from the fiber surface. The two first sequences, S_1 and S_2, are deposited on single fibers, the third S_3 encapsulates a group of fibers and the last one, S_4, acts as an external coating for the whole fiber tow.

When such model minicomposite is loaded beyond the proportional limit, its multilayered matrix undergoes microcracking (the cracks are deflected by the mechanical fuse layers, according to a complex scenario). If the cracks are maintained open, oxygen diffuses along this complex path reacting with the B- and Si-bearing species (depending on temperature) forming a B_2O_3-based fluid oxide phase that heals the cracks, slows down the in-depth diffusion of oxygen and increases the lifetime of the material (Fig. 9).

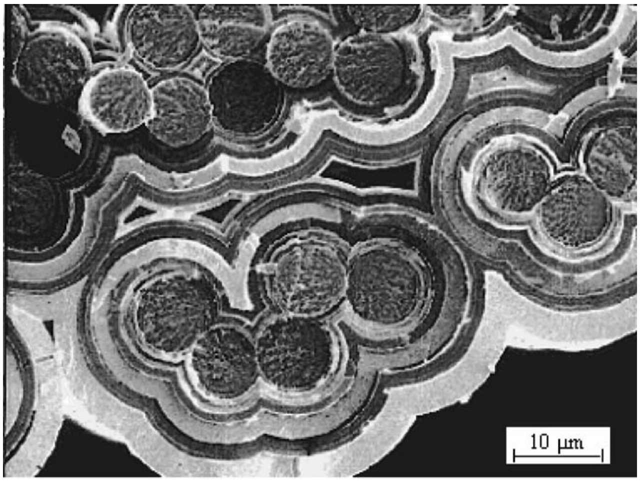

Fig. 9. Cross-section of a model minicomposite with a self-healing multilayered matrix deposited within a fiber tow by P-CVI [14].

5. Conclusion

Boron-bearing species can be advantageously introduced in non-oxide ceramic matrix composites to improve their oxidation resistance. B-doped pyrocarbon and hex-BN interphases display a layered crystal structure similar to that of pyrocarbon itself and then can be used to deflect matrix cracks (acting as mechanical fuses) with an improved oxidation resistance. Further refractory boron compounds compatible with the ceramics involved in composites, such as boron nitride, boron carbide, and boron silicides, form B_2O_3–based fluid phases when exposed to an oxidizing atmosphere that exhibits healing properties in a broad range of temperature. This property has been used to design multilayered interphases and matrices which give an improved oxidation resistance to ceramic matrix composites which become thus potential material candidates for applications in the aerospace field. The approach could be further extended to ceramic fiber themselves.

Acknowledgments

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