Importance of fiber/matrix bonding in SiC/BN/SiC on mechanical and interfacial properties

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SUMMARY : SiC/BN/SiC composites were produced by Chemical Vapor Infiltration of a fiber preform. Three kinds of BN interphases were deposited on the fibers : (i) a poorly organized, (ii) a highly crystallised and (iii) a bilayered interphase with the low organized BN against the fiber followed by the highly crystallized one. The mechanical behavior of SiC/BN/SiC composites was determined under tensile loading at room temperature. The interfacial properties were extracted from stress-strain and fiber push-out test curves. Relationships between the stress-strain behavior and the measured interfacial parameters could be established for the types of BN interphases. Further, trends in the evolution of interfacial properties with the BN structure (and so, with BN interphase processing conditions) were anticipated. A significant effect of the fiber/coating bond strength on the interfacial damage is evidenced. Finally, the efficiency of boron nitride as an interphase is compared to the that of pyro-carbon.

Keywords : boron nitride, interphase, 2D composite, microcomposite, interfacial parameters, tensile test, push-out.

INTRODUCTION

It is now well acknowedged that properties of fiber/matrix interfaces determine the mechanical behavior of brittle-matrix composites [1,2]. Non-linear deformations result from the deviation of matrix cracks into the fiber-matrix interfaces. This phenomenon can be controlled by deposition of a layer of a soft material over the fibers. The most efficient interphase materials are characterized by an anisotropic microstructure (often graphite) and a low shear modulus (around 30 GPa) [3,4]. Two materials are commonly used as interphases in SiC/SiC composites : pyrocarbon and boron nitride. Carbon stays actually the most efficient interphase. However it is very sensitive to oxidation. Oxidation of carbon takes place, from 500°C. Therefore, if the interphase is exposed to oxygen, the carbon coating burns down, removing the transfer of load between the fibers and the matrix. On the contrary, at temperatures above 1000°C, passive oxidation of the SiC matrix occurs. The silica that formed can block up the matrix cracks, thus inhibiting further degradation of interphases [4,5].

The reduction of SiC/SiC sensitivity to oxidation may be obtained by the use of BN interphases [6]. The primary objective of the present paper was to investigate the interfacial characteristics of BN interphases in SiC/SiC composites, and then relationships with features of the stress-strain behavior measured under tension.

The critical importance of interfaces and interphases in the thermostructural performance of ceramic matrix composites dictates the need for straightforward and convenient test methods for measuring their properties and evaluating their damage. Approaches to debonding of a fiber embedded in a brittle matrix during push-out/in or pull-out tests [7-11] have been proposed. They are based on load displacement curves involving either the relative axial displacements of the fiber and the matrix during push-out and pull-out tests [8-11].

Fiber sliding during push-out of the fiber has been analysed in the presence of residual stresses [8,11]. The sliding often involves friction. Other shear lag models have been proposed. They are often restricted to systems involving a radial residual compressive stress acting on the fiber/matrix interface [7-11].

In this paper, correlations between mechanical behaviors of 2D composites and the nature of BN interphases are proposed on the basis of their respective interfacial properties derived from tensile and/or push-out test curves. Fiber bonding and frictional sliding were investigated by means of push-out tests.

TESTING METHODOLOGY AND ANALYSES

Specimen preparation

SiC/BN/SiC composites were produced by Chemical Vapor Infiltration of a fiber preform [5,12]. They were reinforced with the SiC ex-PCS Nicalon fibers (SiC ex-PCS Nicalon NL 202 fiber from Nippon Carbon, Japan) that have been used either as-received or treated (Proprietary treatment performed by SEP, Bordeaux), (Table 1).

Ref.	Number of BN layer	BN degree of crystallization	Failure properties			
			ε (%)		σ (MPa)	
			S	T	S	T
BN 1	one	high	0.58	0.06	220	32
BN 2	one	low	0.38	0.11	210	110
BN 4	two	BN 2 + BN 1	0.5	0.65	200	210

Table 1 : Main characteristics of 2D-SiC/BN/SiC from tensile tests (fiber fraction 40 %)
with S : for standard (or as-received) fibers, and, T : for treated fibers

ε : strain, and, σ : stress

Three batches of composites (Table 1) were manufactured under processing conditions that were selected in order to minimize damage of the fibers during processing and to optimize the adhesion of the BN coating to the fiber surface, and the microstructure of BN [12]. Three batches of SiC/SiC composites were manufactured with single (with different degrees of crystallisation) or bi-layered interphases (Table 1).

Mechanical tests

Presentation of push out tests

Fiber bonding and frictional sliding in the SiC/BN/SiC composites were investigated by means of single fiber push-out tests [8,11,13]. The interphase characteristics were extracted from the experimental stress-fiber end displacement curves by fitting the push-out model of Hsueh [11], as discussed in a previous paper [13].
Push-out tests were performed on 500 µm thick wedges prepared using standard metallographic techniques. The tests were conducted at a constant displacement rate of 0.1 µm/sec using the interfacial test sytem. The load was applied to the top of the fiber using a flat bottom diamond cone (Apparatus designed by ONERA, Chatillon, France).

Presentation of tensile tests on 2D composites

The stress-strain behavior of the SiC/BN/SiC composites was measured under tensile loading conditions (strain rate 0.05 $\%.min^{-1}$). Deformations were measured using an 25 mm gauge extensometer. The dimentions of the 2D composite samples were 3*8*100 mm.

RESULTS

Tensile tests on 2D SiC/BN/SiC composites

The tensile stress-strain curves obtained for the two series of SiC/BN/SiC reinforced with as-received or treated fibers showed that mainly those with a bi-layered interphase exhibited a non-linear domain of deformation extending over a wide range of deformation, and rather large strains to failure (ε^R 0.5 %, and, σ^R 200 MPa), (Table 1, and, Figure 1).

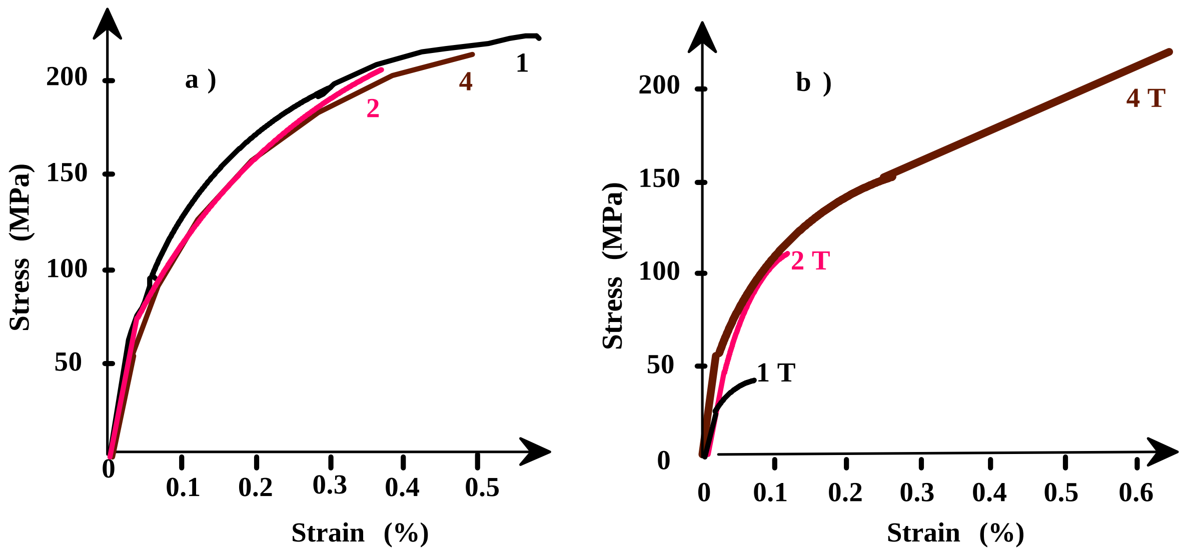

Figure 1 : Strain-stress curves from tensile tests on 2D-SiC/BN/SiC reinforced either with as-received fibers (a) or with treated fibers (b)

Push out tests on 2D composites

The stress-fiber end displacement push out curves exhibit well defined successive steps [7,8] (figure 2) : (i) elastic deformation of the fiber, (ii) debonding and controlled propagation (non-linear part), (ii) a catastrophic debonding (load drop) and then (iv) push-out of the fiber through the matrix with sliding friction (pseudo-plateau). When reinforced with treated fibers, they never had the upward curvature observed for SiC/C/SiC [14,15].

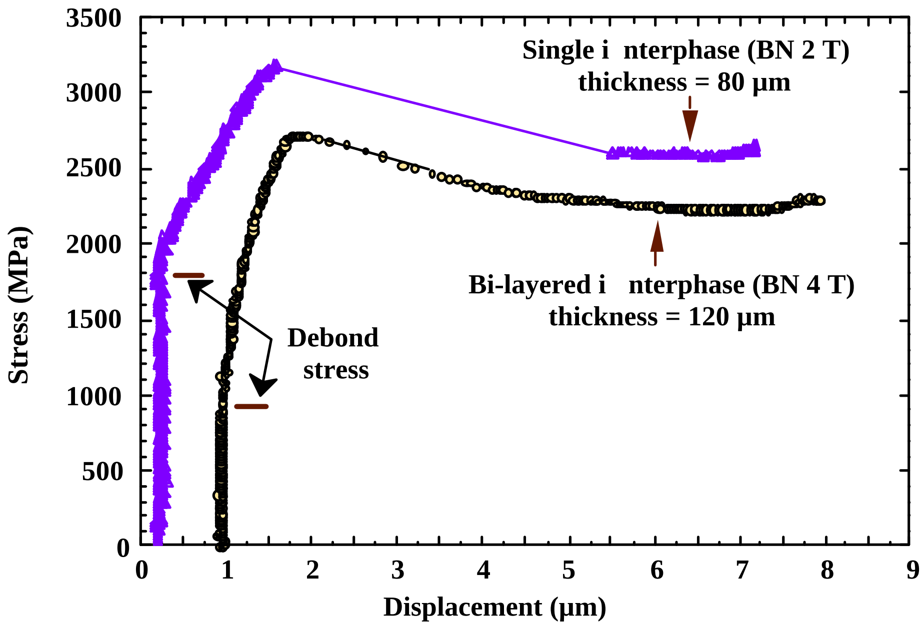

Figure 2 : Push-out curves measured on 2D-SiC/BN/SiC reinforced with treated fibers

Composites reinforced with as-received Nicalon fibers

The stresses to create and then to propagate the debond as well as interfacial shear stresses crack are much higher than those measured on 2D SiC/C/SiC reinforced with as-received fibers [13,14], (Table 2).

Therefore, such interfacial shear stresses may be regarded as rather high. The highest values were obtained for composites with a single BN interphase. The debond stress is insensitive to the condition of BN deposition. The interfacial shear stresses also seem to be insensitive to the condition of processing since identical values were obtained for interphases 1 and 2 that were deposited under opposite conditions. However, the lowest interfacial shear stress corresponds to interphase made of two layers of BN with the second one processed under the most aggressive conditions for the fiber. It is worth mentioning that a lower roughness amplitude was estimated for this interphase 4.

On the other hand, in the composite with the interphase 2, the effect of the friction seems to be the most efficient as reflected by the high applied maximum stress, the short fiber-end displacement and the roughness amplitude.

SEM examination of the sliding surfaces reveals that for a bi-layered BN interphase the debond is preferentially located between the BN layers, otherwise it occurred at the fiber/coating interface. However, for BN1, the fiber surface was quite rough and the matrix surface showed a lot of hollows, whereas for BN2, the slid surface is very smooth, as usually observed in such composites [14-18].

Ref. BN	Sample thickness (µm)	Debond stress (MPa)	Maximum stress (MPa)	Displa--cement (µm)	τ plateau (MPa)	Interfacial properties [6] τ (MPa)	μ	σ_C (MPa)	σ_Z (MPa)	Roughness amplitude (µm)
1 S	200 (10)	1130 (200)	3700 (1300)	1.35 (0.3)	66 (10)	87 (22)	0.11 (0.02)	-560 (220)	-730 (230)	32 (14)
2 S	90 (15)	1250 (200)	3800 (500)	1.0 (0.2)	95 (20)	83 (15)	0.09 (0.03)	-510 (160)	-1020 (330)	45 (20)
4 S	160 (50)	1200 (300)	2700 (800)	1.1 (0.6)	48 (10)	41 (13)	0.09 (0.03)	-610 (340)	-490 (160)	16 (10)
2 T	60 (15)	2000 (440)	2800 (350)		140 (26)					
4 T	120 (10)	740 (100)	2700 (300)	0.9 (0.1)	77 (10)	66 (5)	0.06 (0.01)	-320 (80)	-1200 (60)	68 (7)

Table 2 : Interfacial characteristics extracted from push-out curves measured on 2D-SiC/BN/SiC
with S : for standard (or as-received) fibers, and, T : for treated fibers,
τ : the interfacial shear stress, μ : the friction coefficient, σ_C : clamping residual stress,

σ_a : axial residual stress, $\tau_{plateau}$: interfacial shear stress calculated from stress for the whole sliding of the fiber, and, (standard deviation)

Composites reinforced with treated Nicalon fibers

A high debond stress was estimated for interphase BN 2T only (σ_d = 2000 MPa, Table 2). It is much larger than those estimated for the composites reinforced with untreated fibers. Unfortunately, interfacial properties could not be extracted from the non-linear domain of the push-out curve, owing to bending of the sample. The interfacial shear stress that was extracted from the plateau is quite high (τ 140 MPa).

Lower interfacial shear and debond stresses were obtained for the bi-layered interphase (BN 4T, interphase made of two BN layers whom the first one against the fiber is identical to this one of BN 2T) (Table 2). These shear stresses are close to those measured on the composites reinforced with untreated fibers. The magnitudes of debond stresses may explain the stress-strain behavior displayed by composites 2T and 4T. Premature failure of the composite 2T may may be attributed to the high σ_d value. The stress-strain behavior of 4T that is similar to the one observed for the composites reinforced with untreated fibers may be attributed to the comparable magnitude of τ and the low value of σ_d.

The observation by scanning electron microscopy revealed that debonding took place at the fiber/BN interface in composite 2. So, the debond stress is related to interfacial bond strength (σ_d 2000 MPa). Moreover, the coating appeared to be not continuously in contact with the fiber along this interface owing probably to a phenomenon of attack of the fiber by the gaseous phase.

In composite BN 4T, bonding occurred in the interface between two BN layers. Figure 3 shows that one BN sublayer (BN sublayer remains bonded to the fiber whereas a second layer (double arrow) can be observed on the matrix.

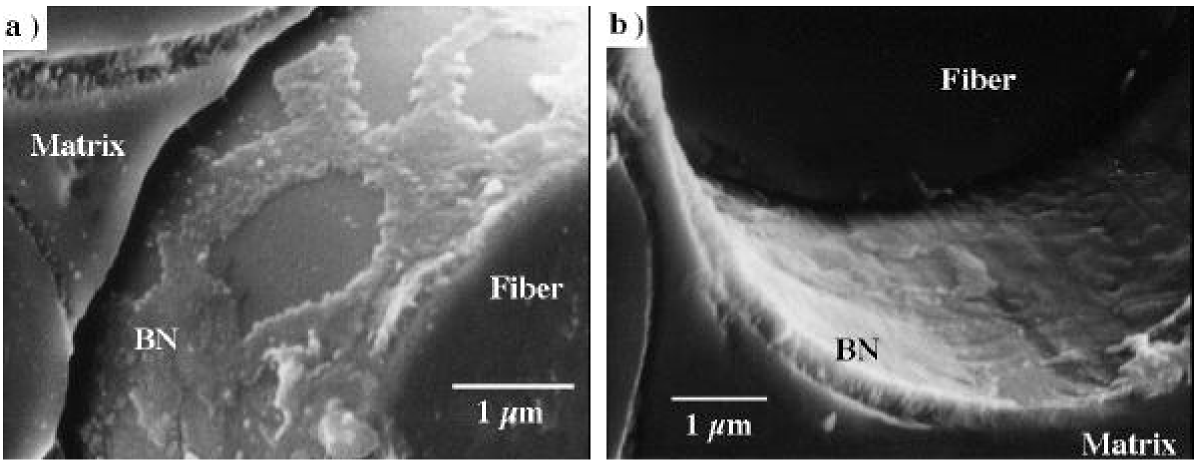

Figure 3 : SEM micrographs showing the sliding surfaces during push-out tests performed on the 2D-SiC/bi-layered BN/SiC composites reinforced with treated fibers :

a) fiber surface with the low-crystallized BN layer, and, b) matrix side with the highly crystallized BN layer.

SEM examination of fracture surfaces in 2D specimens tested under tension also shows the presence of BN coating remaining stuck to the fiber. The BN repartition over the fiber surface has a shape of waves, as already observed during push-out tests.

DISCUSSION

Stress-strain behavior of SiC/BN/SiC composites

The debond stress in composite BN 2 is quite high (σ_d = 1500 MPa), as well as the interfacial shear stress (τ = 90 MPa). These data reflect high load transfers through the interphase, which may explain that the fiber could not be pushed out the matrix despite a thin sample thickness.
The use of treated fibers seemed to strengthen the fiber/coating bond for the composite with the interphase 2T (as shown by σ_d = 2000 MPa) and 4T (first coating against the fiber similar to BN 2T and remaining bonded to fibers after debonding).
In the composites BN 4 and BN 4T, debonding occurred along the interface between sucessive BN sublayers, which is characterized by a low shear stress when comparing with the other tested SiC/BN/SiC for which debonding took place in the fiber/BN coating interface. These features indicate that the interface between successive BN sublayers was weaker than the fiber/BN coating bond and actually acts as mechanical fuse.

The tensile behavior of the 2D SiC/BN/SiC composites was in excellent agreement with the interfacial properties measured using push-out tests, since close interfacial shear stresses for the composites that exhibited comparable stress-strain behaviors, whereas the highest debond and interfacial shear stresses were observed for composite BN 2T that experienced premature failure.
For the condition of deposition (2), the coating was shown well adherent to the fiber [12]. The corresponding debond stress, interfacial shear stress and resistance to propagation of interfacial crack were higher when comparing with the other composites (1 and 4) suggesting an efficient load transfer during a tensile loading. The composite experienced a premature failure whereas the microcomposites exhibited a high strain at saturation. Both features reflect efficient load transfers. Failure of 2D composites involve additionnal phenomena, including variability in fiber strength degradation during processing.

The composites with an interphase processed in aggressive conditions (1) for the fiber possessed a weaker fiber/coating bond. The propagation of cracks along the fiber surfaces was easier than for the composite (2). This is indicated by the stress-strain tensile curve determined on microcomposites, which displays a plateau-like feature when compared with microcomposite 2. This feature was not observed with the 2D composite. Furthermore, microcomposite 1 failed at a low deformation, which may be attributed to a degradation of the fiber during processing.

For the condition of deposition (4), an interphase with two BN sublayers was obtained, involving a weak interface between the BN sublayers. Thus, the debond can occur partially in the interphase. The associated low interfacial shear stress is consistent with the stress-strain behaviors measured on the 2D composite (lower stresses) and on the microcomposites (plateau-like behavior).

Comparison with other SiC/BN/SiC composites

For comparison purposes, this push-out testing technique was also applied to composites processed with as-received Nicalon fibers but different boron nitride interphase (developed by S. Prouhet [15,16]), that displayed identical stress-strain behaviors. Similar interfacial characteristics were obtained. These shear stresses are consistent with those determined for the composites prepared for the present study.

Results from the push-out tests performed on these composites [17] showed that increasing thickness of the boron nitride interphase trends to cause a degradation of the interfacial shear stress. The shear stresses fall into the same range as those measured on the materials prepared in the present study.

The interfacial shear stresses may be satisfactorily compared to the tensile stress-strain behaviors. Thus, the lower interfacial shear stress was measured on the material that displayed a plateau like behavior. The interfacial shear stresses for materials, exibiting the same tensile behaviour, are similar.

Comparison with SiC/C/SiC composites

For the two series of SiC/BN/SiC reinforced with as-received or treated fibers, the wide range of deformation, and large strains to failure (ε^R 0.5 %, and, σ^R 200 MPa), obtained from the tensile stress-strain curves (Table 1), remain low in regard to those of SiC/C/SiC reinforced with either as-received (ε^R 1 %, and, σ^R 200 MPa) or treated (ε^R 1 %, and, σ^R 300 MPa), [18] .

Whatever the fibrous reinforcement in SiC/BN/SiC, stresses to create and then to propagate the debond as well as interfacial shear stresses (τ between 50 and 90 MPa, with μ 0.1), (Table 1), are much higher than those measured on 2D SiC/C/SiC reinforced with as-received fibers (τ < 20 MPa, with μ 0.02) [14,15], but remain lower than those of SiC/C/SiC reinforced with treated fibers (τ between 100 and 300 MPa, with μ 0.15). When reinforced with treated fibers, they never had the upward curvature observed for SiC/C/SiC [14,15], with a branching of the interfacial crack inside the interphase. Such a deviation within the interphase of SiC/C/SiC composites is already observed for single C interphase, with thickness as thin as 0.1 µm.

Finally, in SiC/BN/SiC composite, the deviation of matrix cracks within the interphase was observed in the presence of a weak interface in the interfacial sequence. From this viewpoint, single layered BN coatings were not found as efficient as carbon interphases as they showed less sensitivity to delamination under a shear stress.

CONCLUSION

The interfacial characteristics were measured using microindentation tests performed on 2D-composites. Comparable stress-strain behaviors were found to correspond to closely related interfacial properties. Correlations were also established between the conditions of BN-processing and interfacial properties derived from push-out tests. Interfacial characteristics were generally higher than those determined for SiC/C/SiC materials reinforced with as-received fibers.

When the BN interphase is made of two successive sublayers, the interface between the BN sublayers is the weakest point. Debonding was observed in this interface. This mechanism becomes essential when the fiber/coating bond is strengthened by using treated fibers. A single boron nitride coating does not seem to be as efficient as a carbon coating, since it did not show a tremendous ability to delamination to promote deviation of the matrix crack within the interphase.

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