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The interphase and interface microstructure and chemistry of isothermal/isobaric chemical vapour infiltration SiC/BN/SiC composites: TEM and electron energy loss studies

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The boron nitride interphase and its interfaces in two-dimensional-SiC/BN/SiC composites have been analysed by transmission electron microscopy and electron energy loss spectroscopy. BN was deposited by isothermal/isobaric chemical vapour infiltration from BCl_3–NH_3–H_2 mixture at moderate temperature. BN and the fibre/BN interface exhibit different features depending on the nature of the Nicalon^{TM} fibre surface, raw or treated prior to the BN deposition. When untreated fibres are used, a carbon-rich layer and silica clusters are formed during the manufacturing of the composite. In that case, the interphase is poorly organized and presents a porous microstructure and a large carbon content. With the treated Nicalon^{TM} fibre, no formation of a new interlayer is observed at the fibre–BN interface and the interphase exhibits a better organized turbostratic microstructure with no voids. Additionally, in both types of composites, a carbon-rich layer is formed at the BN–matrix interface during the SiC infiltration step at about 1000 °C.

1. Introduction

During the past decade, many studies have reported the importance of the fibre coating in controlling the mechanical behaviour of ceramic matrix composites (CMC) [1–5]. All these works have established that their mechanical properties can be improved by adjusting the fibre–matrix (F/M) bonding to deflect the microcracks that are produced in the brittle matrix under loading, from mode I (perpendicular to the fibre) to mode II (parallel to the fibre axis).

High mechanical properties in a non-oxidizing atmosphere have been obtained when SiC or SiC(O) fibres, particularly Nicalon^{TM} (Nippon Carbon, Japan) fibres, were embedded into glass-ceramic matrices [6]. In this case, the non-brittle properties have been attributed to a carbon-rich layer which is formed *in situ* between the fibre and the matrix during the composite fabrication. In systems where this layer is not formed *in situ*, like SiC/SiC, the fibres can be coated by a graphitic carbon prior to the matrix deposition [7, 8]. Moreover, improved mechanical properties have been obtained when the anisotropy of pyrocarbon is increased [9]. Unfortunately, composites with a carbon-rich interface exhibit low strength and toughness when exposed to a high-temperature oxidizing environment for a long time [4, 10]. In particular, when a threshold stress is applied, microcracks occur in the matrix and oxygen can diffuse to the fibre–matrix interface. The result is either a very weak F/M bonding when carbon is consumed leading to a decohesion, or a strong link when a glassy oxide layer forms [10]. Because of its similar layer structure and its better resistance to oxidation, boron nitride instead of carbon has been proposed as a possible solution [11, 12].

BN coatings can be engineered either by chemical vapour deposition (CVD) or isothermal/isobaric chemical vapour infiltration (ICVI) to achieve the expected structural organization and anisotropy necessary to improve the mechanical behaviour as well as the oxidation resistance. Several studies have been carried out to characterize the BN interphase and the interfaces in ceramic and glass-ceramic matrix composites [11–15]. Two well-defined amorphous sublayers of carbon and silica were observed in Nicalon^{TM}/BN/SiC composites when boron nitride was deposited by ICVI from a BF_3–NH_3 mixture [12]. Sun *et al.* [13] detected a very thin carbon-rich interface (5–10 nm) between the fibre and the BN interphase in SiC/BN dual-coated Nicalon^{TM} fibre in a BMAS matrix. In this case, boron nitride was deposited by CVD using a 3M proprietary precursor at about 1000 °C. Bender *et al.* [14] observed the interface between two types of SiC fibres, Nicalon^{TM} and Tyranno^{TM}, (UBE Industries, Japan) and a BN interphase deposited by CVD from BCl_3 and NH_3 at 970 °C. In both cases, a carbon-rich reaction layer is formed at the fibre/BN interface. Furthermore, in Tyranno^{TM}-based composites, TiC crystallites are also formed in the carbon layer. Naslain has shown that the formation of this carbon-rich interface is due to the decomposition of the oxygen-rich SiC fibres at high temperature [11]. In fact, the composite fabrication mainly requires temperatures equal to or higher than 1000 °C, especially for glass-ceramic densification. Then, the successive steps of the composite processing may change the characteristics of each component and consequently the thermomechanical and chemical properties of the material. Finally, high-strength composites require adequate choices of the fibre, and a careful control of its surface treatment before and during the interphase and the matrix elaboration steps.

In this paper, we describe the results of recent efforts to control the interfacial chemistry and microstructure of Nicalon^{TM} fibre-reinforced SiC matrix composites with a BN interphase. Different SiC(O) fibres have, therefore, been coated with boron nitride, by ICVI at moderature temperature from a BCl_3–NH_3–H_2 mixture. This study has been extended to the determination of the chemical and structural changes that may occur in the BN coating and at its interfaces. The microstructures were studied by transmission electron microscopy (TEM) allowing micro-chemical analyses by electron energy loss spectrometry (EELS).

2. Experimental procedure

The composites were prepared from two-dimensional preforms (180×80×3 mm^3), consisting of stacks of fabrics made with Nicalon^{TM} fibres maintained pressed together with a graphite tooling. Several studies have reported that the ex-PCS SiC(O) Nicalon^{TM} fibre consists of SiC crystals of about 3 nm in size embedded in a silicon oxycarbide amorphous matrix containing, in addition, some free carbon and traces of hydrogen [16–18]. The surface is often contaminated by silica forming a thin and irregular film (13–20 nm thick) [8, 10, 16]. To prevent damage by handling, the fibres usually received an organic size that was thermally decomposed before the deposition stage in our case.

Two different series of Nicalon^{TM} fibres were used. The first set consisted of untreated NLM 202 fibres already described above whose surface is irregular and composed of silica with some amount of free carbon [8, 10, 16]. The second one consisted of fibres which have been submitted to a treatment performed by the Société Européenne de Propulsion (SEP) (proprietary treatment). The treated fibre presents a different composition over a significant thickness and the surface is now more regular, and rich in free carbon [8]. It has been verified that this treatment does not damage the mechanical properties of the fibres.

The graphite tooling fulfils two functions. It maintains the stack of Nicalon^{TM} fabrics at a constant thickness, and its geometry allows the gas-phase composition all along the fibrous preform to be homogenized. In this way the uniformity of the deposit is improved.

The BN interphase was infiltrated within the porous preforms according to an ICVI process from BCl_3–NH_3–H_2 mixtures. The process was carried out at a moderate temperature ($\leqslant$850 °C) and reduced pressure in conditions that are described elsewhere [19]. The SiC matrix was then elaborated by ICVI from methyltrichlorosilane (MTS)–hydrogen mixtures, at about 1000 °C.

The interfacial microstructures were studied by transmission electron microscopy (TEM), whereas micro-chemical analyses were achieved by electron energy loss spectrometry (EELS). These experiments were performed on a Philips CM30ST microscope fitted with a Gatan 666 spectrometer. Because of its low Z-element sensitivity, EELS is particularly suitable for the study of this type of material at nanometric level. It is possible to characterize the samples by the observation of core electron excitation and also of plasmons. These two types of information are used for the qualitative and quantitative analysis of the different elements present in the material.

In this study, our interest focused on boron, carbon, nitrogen, oxygen and silicon elements. They are characterized by 1s electron excitation occurring at about 188, 284, 401 and 532 eV for boron, carbon, nitrogen and oxygen, respectively, whereas in this energy range, silicon is characterized by a 2p electron excitation at about 99 eV. EELS analyses have been performed using a probe size on the sample of about 20 nm diameter. It could be reduced to 7 nm for the characterization of thin sub-layers. The energy resolution of the spectrometer was about 1.5 eV.

More precise chemical information can be deduced from the fine structures or from the chemical shift of the associated excitation edges. In particular, when silicon is involved in SiC or in SiO_2, the shift of the $L_{2,3}$ edge is about 4 eV, which is associated with a significant change of the silicon near-edge structures [20, 21]. Similar information can be deduced from the exploitation of the low-loss spectra which concern the plasmon and interband transitions. In this case of carbon and boron nitride, they are characteristic of the structure, either diamond, or graphitic or amorphous for both materials [22].

The samples from tensile-tested specimens have been extracted at two different positions, near the failure surface and in the foot of the sample. Thin foils ($\leqslant$50 nm) were prepared in a conventional way by a mechanical polishing followed by Ar^+ ion milling. For all the samples, the analyses were performed radially, from the fibre to the matrix through the BN interphase.

3. Results

At first the sampling was examined both near the fracture zone and in the foot of a tensile specimen.

Similar results concerning the microstructure and the chemical composition were obtained in these two parts of the sample. The deposit and the interfacial zones appear homogeneous in all the composites. Then in further experiments, only the samples from the foot of tensile bars were studied.

3.1. Two-dimensional SiC/BN/SiC composites with untreated NLM 202 Nicalon^{TM} fibres

Typical features of the interfaces and the BN-interphase in the composite are illustrated in Figs 1 and 2. The presence of an interfacial layer around the SiC fibres is slightly indicated by a brighter contrast. The same contrast effect is observed at the interface between BN and the SiC matrix. The BN interphase and the interfacial layers are successively studied below.

3.1.1. The BN interphase

The thickness of the BN interphase is always constant, about 0.4 μm. Its texture is porous. The pores, about 9 nm diameter, are regularly distributed in the coating (Fig. 2). High-magnification TEM images and electron diffraction patterns reveal a turbostratic and poorly organized structure all along the BN coating. The basic structural units are randomly distributed in the amorphous phase of the deposit.

The EELS spectra (Fig. 3a) taken from this region show boron and nitrogen edges which are typical of these elements when involved in hexagonal boron nitride [22]. In addition, these spectra evince significant amounts of carbon and oxygen in the BN phase. Silicon was below the detection limits of EELS (<1 at %). The concentrations of boron, carbon, nitrogen and oxygen were determined by the classical quantitative analysis method [23], the result of which is an average atomic composition of 34% N, 30% B, 26% C and 9% O. In the plasmon energy loss region (Fig. 3a inset), a peak is observed at about 8.3 eV. It is interpreted as a π plasmon in the hexagonal BN. In the same way, the dominant peak at about 24.5 eV corresponds to a $\sigma+\pi$ plasmon in this material [24].

From these analyses it is concluded that the deposit is not pure hexagonal boron nitride: it contains carbon and oxygen and is slightly boron-poor. Moreover its composition is uniform in the whole interphase.

3.1.2. The fibre–BN interface

This interface corresponds to the thin clear sublayer, 10 nm wide, observed on the TEM image (Fig. 1). Quantitative EELS analysis (Fig. 3b) reveals a carbon-rich sublayer (54 at %), which contains a significant amount of oxygen (32 at %) and some silicon (8 at %) and boron (5 at %). No nitrogen has been detected in this part of the sample. The double peak at 109 and 115 eV of the Si $L_{2,3}$ near-edge structure can be associated with the presence of silica on the surface of the untreated Nicalon^{TM} fibre [20]. As no nitrogen is observed and an oxygen excess is deduced from the EELS treatment, the formation of boron oxide should be considered. Owing to the low boron content and the poor intensity of the boron K-edges, this cannot be confirmed by our experiments.

Along the interface, the EELS spectrum (Fig. 3b) allows us to identify SiO_2 clusters (Fig. 1). These

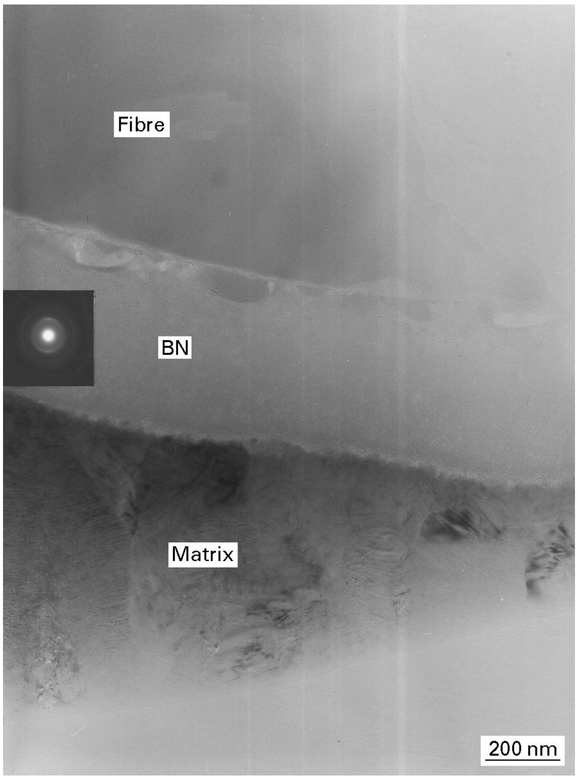

Figure 1 Interfacial zone of a SiC/BN/SiC composite with untreated Nicalon^{TM} fibres and diffraction pattern of the turbostratic BN interphase.

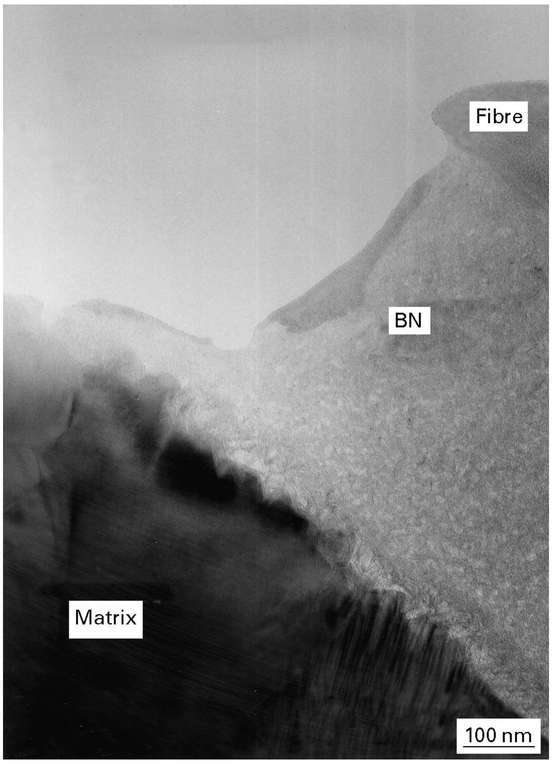

Figure 2 TEM image of the interfacial zone showing the interfaces and the microvoids in the BN interphase deposited on untreated fibres.

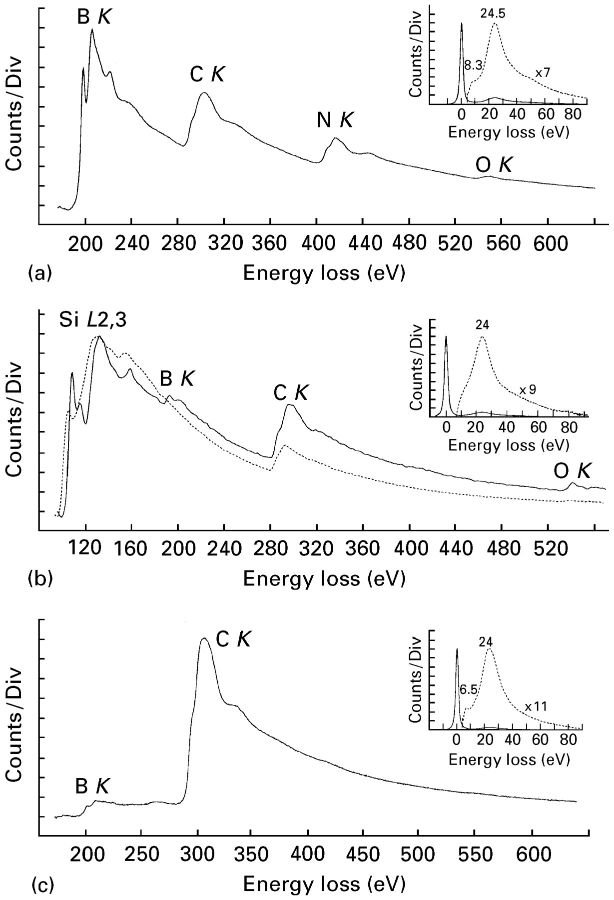

Figure 3 EELS and plasmon (top right inset) spectra of the interfacial sequences: (a) BN interphase, (b) untreated Nicalon$^{\mathrm{TM}}$ fibre–BN interface (- - - SiC spectrum) and (c) BN–SiC-matrix interface.

clusters are more easily observed on the TEM image (Fig. 4). In addition, small amounts of carbon that appear in black contrast on these figures, are distributed around these clusters and deeper in the BN interphase (up to 100 nm). These small domains, 3–10 nm in size, are clearly observed at high magnification. They are made of a stacking of basic planes ($d \approx 0.37$ nm) which lie parallel to the interface, in agreement with the associated electron diffraction patterns typical of textured carbon.

3.1.3. The BN–matrix interface

This interface is thicker than the fibre–BN interface, typically between 30 and 50 nm with strong protuberances in the matrix. Similarly to the other interface, it exhibits a bright contrast (Fig. 2). EELS analysis has revealed a high concentration of carbon with traces of silicon, boron and nitrogen (Fig. 3c). Additionally, the near-edge fine structure of the Si$L_{2,3}$ edge is consistent with Si–C bonds [21]. A π plasmon at 6.5 eV and a $\pi + \sigma$ plasmon at 24 eV are also observed (Fig. 3c inset). They are characteristic of a partially organized hexagonal carbon [20]. This is consistent with the fine structure of the C*K* edge (Fig. 3c) and the high magnification TEM figures.

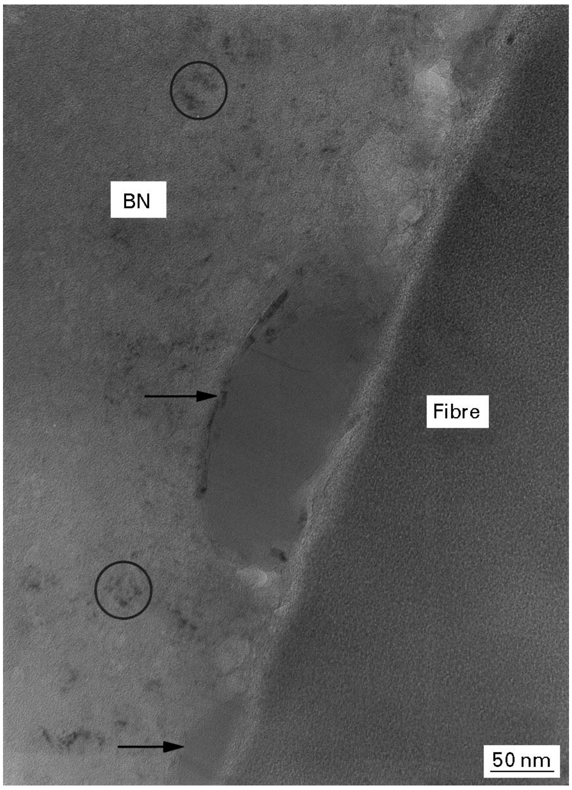

Figure 4 Untreated fibre–BN interface showing (———→) the SiO_2 clusters and (O) the carbon domains.

3.2. Two-dimensional SiC/BN/SiC composites with treated NLM 202 Nicalon$^{\mathrm{TM}}$ fibres

As shown in Fig. 5, three different parts between the fibre and the matrix can be observed as in the previous composite.

3.2.1. The BN interphase

The thickness of the BN interphase is homogeneous and thicker (0.46 μm) than for untreated NLM 202 fibres and no voids are observed. The composition is found to be constant in the main part of the interphase. The average composition is 41 at % N, 39 at % B, 10 at % O and 10 at % C. Close to the SiC matrix, the carbon content increases from 10 at % to 20 at %. The structure of the edge (Fig. 6a) and the electron diffraction patterns are characteristic of turbostratic hexagonal boron nitride. For the whole interphase, the main volume plasmon peak is observed at 24 eV with a π plasmon at about 8 eV (Fig. 6a inset). They confirm a hexagonal BN structure of this coating. However, the π peak is more pronounced near the fibre and the matrix (Fig. 6 a inset). This is associated with a stronger π bonding and, consequently, with a better organized BN lattice on the fibre and matrix sides.

3.2.2. The fibre–BN interface

As shown in Fig. 5, a bright zone about 10 nm thick, borders the fibre. This sublayer is mainly composed of carbon (90 at %) with small amounts of oxygen (<10 at %), boron (<6 at %) and nitrogen (<4 at %).

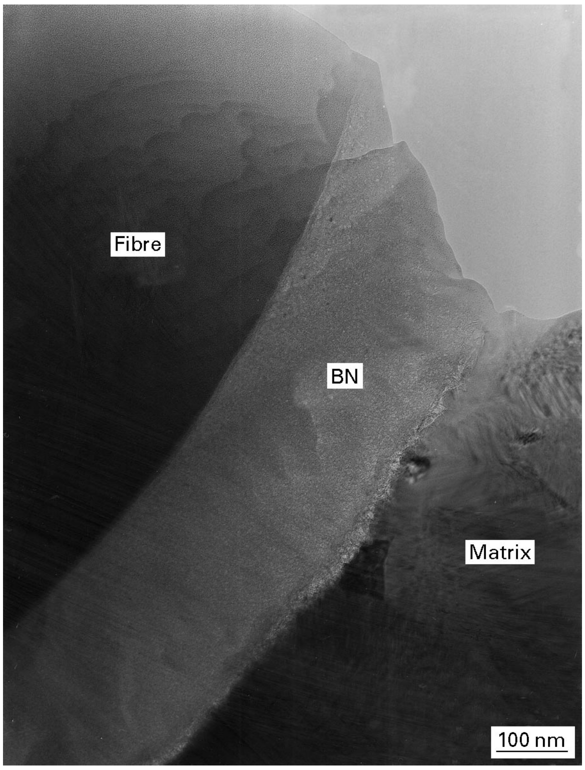

Figure 5 Interfacial zone of a SiC/BN/SiC composite with treated Nicalon^{TM} fibres.

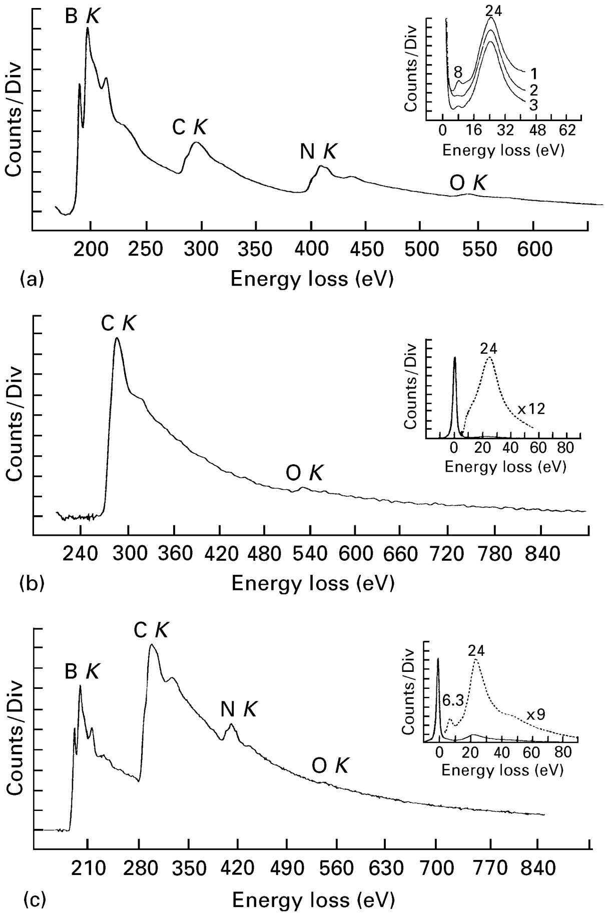

Figure 6 EELS and plasmon (top right inset) spectra of the interfacial sequences: (a) BN interphase inset evolution of the π peak of BN across the interphase from (1) the fibre side to (3) the matrix side, (b) treated Nicalon^{TM} fibre–BN interface and (c) BN–SiC-matrix interface (probe size 7 nm).

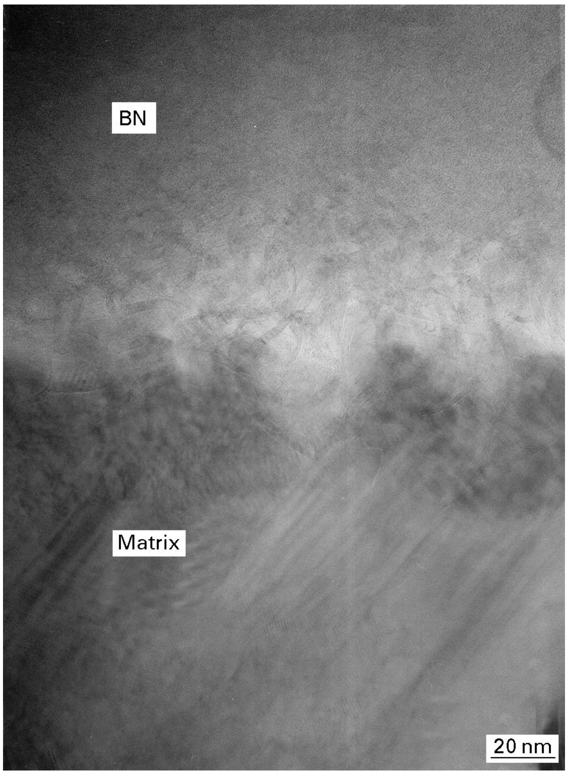

Figure 7 BN–SiC-matrix interface showing the particular feature of the carbon lattice fringes.

In the range of low energy losses, a plasmon peak at 24 eV is observed (Fig. 6b inset). This peak is attributed to the excitation of carbon free electrons. Its position, the absence of a π peak and of fine structures in the C*K* edge (Fig. 6b) are typical of a rather amorphous carbon at the fibre/BN interface. As expected, no silica is observed at this interface.

3.2.3. The BN/matrix interface

Fig. 7 shows the interface between the SiC matrix and the BN interphase. It is coarse and porous with a thickness of about 30 nm. As in the previous composite, this interface is essentially composed of carbon. The fine structure of the C*K* edge (Fig. 6c) as well as the shape of the plasmon peak at 6.3 eV (Fig. 6c inset) and the transmission electron micrographs are characteristic of a fairly well-organized graphitic carbon.

4. Discussion

In this work, boron nitride was deposited by ICVI at moderate temperature and reduced pressure, using a BCl_3–NH_3–H_2 mixture. The BN films always exhibit a homogeneous thickness at different positions in the preform. These results confirm the efficiency of the graphite tooling to homogenize the gaseous phase along the fibrous preform. The BN interphases present a turbostratic microstructure and they are almost stoichiometric with significant amounts of oxygen (9–10 at %) and carbon (10–26 at %).

In the following sections we will examine the influence of the initial Nicalon^{TM} fibre surface on the chemistry and microstructure of the interfaces and the interphase successively.

4.1. The fibre–BN interface

It is now well-established that the Nicalon^{TM} fibre is metastable and that its bulk SiC_xO_y composition is not maintained up to the surface which is mainly composed of silica and carbon [8, 10, 16]. This surface modification might be produced during the last step of the fibre processing. The fibre surface can, moreover, be modified by high-temperature treatments in various gaseous atmosphere [25]. The final interface between the fibre and the interphase can also be changed by the composite processing whatever the infiltration process [26–28].

In our experiments, the ICVI process is carried out in a hot-wall reactor. It has been observed [29, 30] that some intermediate solids can be deposited at the gas entrance where the wall temperature is lower than the deposition one. For BN deposition using BCl_3–NH_3–H_2 mixtures, these solids are mainly ammonium borate hydrates [29, 30] which are highly hygroscopic and consequently a source of oxygen. Some residual oxygen impurity also remains independently from this particular source. That can explain an oxygen incorporation which is always in evidence in BN coatings deposited by CVI or CVD at moderate temperatures from various inlet mixtures [12, 13, 30–32]. On the other hand, a thermochemical decomposition and/or oxidation of the untreated Nicalon^{TM} fibre can arise either during the last step of its processing or during the infiltration stages of BN and of the SiC matrix. Two different fibre/BN interfaces are observed depending on the initial fibre surface.

4.1.1. The untreated Nicalon^{TM}

It appears that the ICVI of BN from BCl_3–NH_3–H_2 mixtures is not very aggressive towards the untreated Nicalon^{TM} fibres because no blistering was observed at the fibre–BN interface. This result confirms the thermodynamic analyses that predict no reaction between the gaseous phase and carbon or silica. Only a moderate interaction was obtained when an Si–C–O mixture was introduced in the calculations, even over a wide range of temperature [19, 33]. On the other hand, a thermal decomposition of the Nicalon^{TM} fibre is not expected at moderate temperature ($\leqslant 850\,^{\circ}C$). However, this phenomenon can arise during the SiC matrix infiltration from MTS–H_2 mixtures at about 1000 °C.

Nevertheless, the presence, close to the fibre surface, of a thin carbon-rich layer containing oxygen and silicon, can be related to the oxidation of the SiC fibre according to the reaction

$$SiC + O_2 \rightarrow SiO_2 + C \qquad (1)$$

As it has been observed, SiO_2 outgrowths are dispersed along the interface between the carbon rich layer and the BN interphase. These irregular sub-layers are consistent with the interface stability criteria of Wagner, which take into account the relative diffusivities of the elements at the interface [34]. If Reaction 1 occurs during the ICVI process, the solid-state displacement leads to the solid products, SiO_2 and carbon. In such a ternary or higher order system, planar interfaces between discrete phases are a special morphology that depends on the relative diffusion rates only. Here, the irregular silica formation could be consecutive to the slower diffusion of silicon atoms through the carbon-rich sub-layer, relative to the diffusion of oxygen atoms which would be in excess at the interface. In that case, the oxygen activity might be high enough to involve a competition between Reactions 1 and 2 with both carbon and CO formation

$$2SiC + 3O_2 \rightarrow 2SiO_2 + CO_{(g)} \qquad (2)$$

Similar composites that contain a BN interphase infiltrated from a BF_3–NH_3 mixture present a continuous silica layer even before the SiC densification step [12, 28]. This difference could be explained by a higher diffusion rate of silicon atoms through the carbon-rich layer due to the higher deposition temperature of BN from BF_3–NH_3 mixtures (about 1000 °C [12]). In this case, Reaction 1 is limited by the oxygen supply, the interface is stable and C/SiO_2 double layers can grow. Then, the SiC infiltration step only enhances the thickness of the double layer as the oxygen atoms have to diffuse through the silica layer. This phenomenon seems to be correlated to the decrease in the oxygen content in the BN interphase [12, 28].

The comparison of these results would confirm that the growth mechanism of the interlayers depends on both the deposition temperature and the duration of the infiltration stages. These two parameters mainly govern the diffusion rate and availability of the various elements at the fibre interphase interface.

4.1.2. The treated Nicalon^{TM}

The treatment of the Nicalon^{TM} fibres leads to a residual carbon-rich layer on the fibre surface. The gaseous phase would not react with the fibres at the earlier stage of the BN infiltration process as there is no direct contact with the SiC_xO_y bulk. Moreover, the carbon overlayer seems to prevent silicon diffusion from the fibre. Contrary to the composite manufactured with untreated fibres, no silicon atoms have been detected in the carbon-rich layer which would act as a diffusion barrier, at least for silicon. This carbon-rich layer seems mainly contaminated by oxygen (10 at %). Such a content is comparable to the oxygen amount in the other components, such as the fibre (12 at % [12]) and the BN interphase (9–10 at %). The carbon-rich layer resulting from the fibre treatment does not appear to be highly oxidized during the composite fabrication as shown by the experimental results where a carbon layer remains at the fibre/BN interface. On the other hand, the oxidation of the bulk fibre is limited, and the formation of any C/SiO_2 double layer does not occur.

4.2. The BN interphase

The different behaviour of the untreated and treated Nicalon^{TM} fibres towards the CVI processing could also explain the differences in the composition and the microstructure of the BN interphase. The formation of voids and the higher incorporation of carbon that are observed when BN is deposited on untreated fibres could be related to some CO formation. The BN interphase deposited without extended interaction with the treated fibres exhibits three times less carbon and no voids when compared to the interphase deposited on the untreated ones.

It appears to be obvious that the organization of the BN lattice is also different for the two types of composites. On the smooth surface of the treated fibres, the BN interphase exhibits a relatively good organization. Furthermore, the evolution of the microstructure in the whole BN coating is in agreement with the results obtained on three-dimensional-carbon preforms that are reported elsewhere [35]. On the contrary, the roughness of the untreated fibre surface, the thermal decomposition and oxidation of the fibre, together with some CO formation, might be detrimental to the BN growth.

Although, for both composites, the carbon content is different, oxygen has been found to be present in similar quantities in the BN interphase. Dugne *et al.* [12] have reported that the oxygen amount in the BN interphase infiltrated from BF_3–NH_3 mixture decreases from 10–15 at % to values lower than 5 at % during the SiC infiltration from MTS-H_2 at about 1000 °C. Moreover, they found no extended interaction zone between the BN interphase and the SiC matrix. It was then interesting to observe more particularly the influence of the SiC infiltration on the BN interphase and the BN/matrix interface microstructures.

Treated Nicalon^{TM} preforms have been infiltrated with boron nitride but without a subsequent SiC infiltration step. The microstructure of the boron nitride has been characterized by TEM and plasmon energy loss. These two analyses do not reveal noticeable differences with the interphase in the treated Nicalon^{TM}/BN/SiC composite. The boron nitride is turbostratic and exhibits a better organization close to the interfaces with the fibre and the matrix. It also presents the same composition as the BN interphase in the corresponding composite. It is almost stoichiometric with similar contents of oxygen (9–10 at %) and carbon (10 at %). On the other hand, no particular composition gradient has been found in the whole deposit and especially no increase of the carbon content has been observed in the external part of the layer. Hence, in contrast to Dugne *et al.*'s results [12], oxygen content is not lowered in accordance with the presence of a single-carbon layer at the fibre–BN interface. The carbon-rich interface between the BN and the matrix appears to be formed during the SiC deposition stage.

4.3. The BN–matrix interface

The carbon-rich formation appears consistent with the thermodynamic calculations performed for the system CH_3SiCl_3–H_2 under conditions simulating the matrix densification [36]. Depending on the H_2/MTS ratio, different deposits can indeed be obtained. As discussed by Christin *et al.* [36], low ratios lead to C + SiC products and high ratios to Si + SiC. However, kinetic considerations revealed the unfavourable deposition of carbon compared to silicon carbide [37]. Moreover the infiltration conditions employed here are known to permit the deposition of stoichiometric SiC [12, 15]. The formation of the porous carbon layer might, therefore, be explained either by the initial solid–gas interaction at the beginning of the SiC infiltration stage, or by a solid decomposition.

It has been shown elsewhere [38], in accordance with several authors, that BN deposited at moderate temperature exhibits a poor stability in moisture [29, 30]. Then, even if BN is a thermodynamically inert substrate with respect to the gas phase involved in the CVI of the SiC matrix [12], oxygen and/or oxide and hydroxide compounds can interact with the gas phase at the beginning of the SiC infiltration.

Another explanation has been proposed by Maniette [39] and Cojean [16] for a similar carbon formation observed in Nicalon^{TM}/SiC composites. Considering the fairly good interlayer spacing for the hexagonal carbon ($d_{002} \approx 0.35$ nm) and the high local anisotropy of the microstructure with layers that tend to be perpendicular to both the matrix and the interphase, they suggested that this carbon interface was due to the decomposition of the SiC crystals at the earlier stage of the matrix deposition. This decomposition which would take place at relatively moderate temperature could be favoured either by an oxidizing or a reducing atmosphere. It must be noted that this porous carbon-rich layer has been reported only when untreated Nicalon^{TM} fibres were coated directly with SiC from a MTS–H_2 mixture. It is now well known and it has been previously shown that the untreated fibre is metastable and decomposes in carbon and silica. That was also confirmed by the results of Maniette and Cojean who observed an irregular silica layer.

Finally, if the formation of this carbon-rich layer at the BN–matrix interface cannot be asserted at the present time, it seems that it is favoured when unstable substrates and/or oxygen-containing interphases are used.

5. Conclusion

The isothermal chemical vapour infiltration process has been successfully used to fabricate boron nitride interphases in two-dimensional Nicalon^{TM}/BN/SiC composites. The experimental infiltration conditions, including an appropriate tooling that holds the fibrous preform, permit a fairly good thickness homogeneity to be obtained. The BN interphases are turbostratic and stoichiometric in boron and nitrogen with constant amounts of oxygen and various amounts of carbon.

The initial fibre surface influences not only the nature of the interface between the Nicalon^{TM} fibre and the interphase, but also the final BN microstructure. The untreated fibres present an irregular surface composition which is different from the bulk. The deposition process leads to the growth of this sub-layer which is mainly a mixture of $C+SiO_2$ irregularly overcoated with large SiO_2 outgrowths. In that case, the BN lattice organization is poor. This feature is expected to prevent good mechanical properties if this interface is the weakest link of the composite. On the other hand, treated Nicalon^{TM} fibres whose surface is smooth and composed of carbon, permit a better organization of boron nitride.

The microstructure of the boron nitride deposited on treated Nicalon^{TM} fibres changes as a function of the radial position in the interphase. A better organization has been found near the interfaces with the fibre and the SiC matrix. As similar results have been observed on various BN-coated fibres before a matrix deposition, this particular feature cannot be attributed to the ICVI processing of the SiC matrix.

Finally, the matrix deposition using MTS-H_2 mixture at high temperature induces the formation of a carbon-rich interface on the matrix side that could be due to the presence of oxygen, particularly in the external part of the BN coating which is not very resistant to moisture. This latter point has often been mentioned when BN was deposited at moderate temperature, especially for CVI processes. An attempt to improve the stability of such deposits is described elsewhere [38]. Finally, from a mechanical point of view, the formation of all the carbon sub-layers should be avoided as the SiC/BN/SiC composites are under investigation for use at high temperature in an oxidizing environment.

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