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**Article title:**

**Multilayered BN coatings processed by a continuous LPCVD-treatment onto Hi-Nicalon fibers**

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**Running title:**

Continuous LPCVD-processing of multilayered BN coatings

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**Abstract:**

Boron nitride coatings were deposited onto SiC fibres by means of a continuous low pressure chemical vapour deposition (LPCVD) treatment from  $\text{BF}_3/\text{NH}_3$  mixtures. This process lies in unrolling the fibre in the reactor axis. The relationships between the processing parameters and the structure of the BN deposits are presented. Thanks to a temperature gradient present in the reactor, multilayered BN films can be performed by stacking successive isotropic and anisotropic sublayers. Tensile tests show that, when the temperature profile is well-adapted, the SiC fibres are not damaged by the LPCVD treatment.

*Keywords:*

LPCVD, boron nitride, structural anisotropy, thin layer, fibre, temperature gradient

## INTRODUCTION

SiC/SiC ceramic matrix composites (CMCs) have been developed for thermomechanical applications. In order to achieved a good toughness, the addition of a thin film (thickness  $< 0.5 \mu\text{m}$ ) of a compliant material called "interphase" between the fibre and the matrix is required [1]. Hence, the interphase allows to optimise the fibre/matrix coupling. Owing to its structural anisotropy, pyrolytic turbostratic boron nitride processed by low pressure chemical vapour deposition (LPCVD) can play such a role [2].

On the one hand, Hinke *et al.* have shown that BN-films can be prepared continuously onto carbon fibres by a continuous CVD-process using the reaction of  $\text{BCl}_3$  with  $\text{NH}_3$  at temperatures ranging from  $700^\circ\text{C}$  to  $1000^\circ\text{C}$  [3]. But with these conditions, BN is expected to be poorly organised and remains isotropic. Nevertheless, we have demonstrated before that the use of such a continuous process in which the fibre is unrolled in the reactor axis allows to treat important lengths of fibres [4].

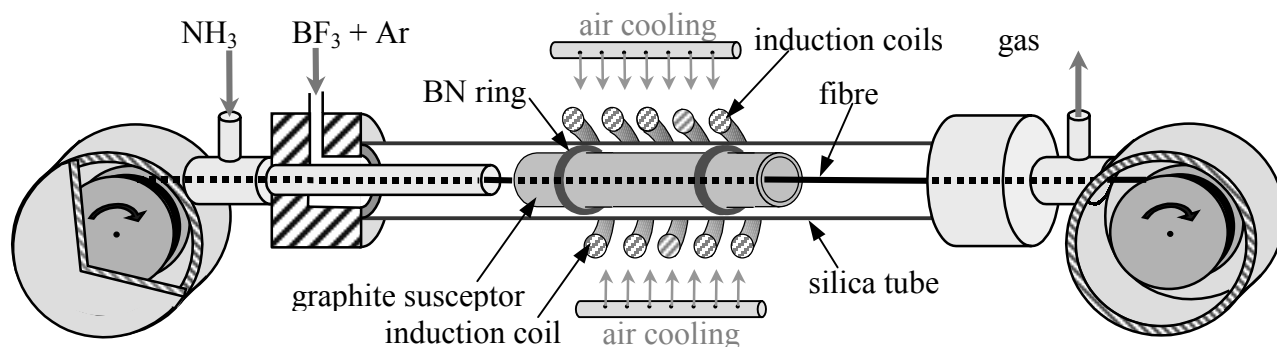
On the other hand, it is possible to obtain a highly crystallised BN by CVD from the  $\text{BF}_3\text{-NH}_3$  gaseous system, but this processing requires to protect the SiC fibre from a chemical attack with an isotropic BN pre-coating obtained with less aggressive conditions [5 - 6]. Thus, in the case of a classical static isothermal CVD, such a multilayered BN film must be infiltrated by following several separate stages (i.e. changing the boron precursor gas and CVD parameters during the experiment...).

The aim of the present paper was to coat SiC fibres with BN films containing at least one anisotropic sublayer by using a one-step continuous dynamic LPCVD-process from the  $\text{BF}_3\text{-NH}_3$  system without damaging the SiC fibre.

## EXPERIMENTAL PROCEDURE

### *Processing*

The BN coatings were processed by LPCVD. They were deposited around each filament of a Hi-Nicalon fibre tow (from Nippon Carbon, Japan). The reactor was a hot wall furnace: a graphite susceptor (length: 35 cm) placed inside a silica tube (inner diameter: 24 mm) is heated by induction. For continuous dynamic study, the fibre tow was unwound from a first spool through the susceptor. The reactor outlet winding around a second spool controlled the fibre travelling rate  $r$  (Fig. 1). For static study, the fibre tow was motionless ( $r = 0$ ).  $\text{BF}_3$  and  $\text{NH}_3$  were the BN gaseous precursors, argon was used as the gas vector but also to dilute the reactive species.  $\text{BF}_3$  and  $\text{NH}_3$  were separately introduced in a cold area of the reactor and mixed near the entrance of the hot susceptor. The total gas flow rate  $Q$  was  $100 \text{ cm}^3 \text{ min}^{-1}$  and the ratio  $Q_{\text{Ar}}/(Q_{\text{BF}_3}+Q_{\text{NH}_3})$  was 0.1. The initial gas composition was determined by  $\alpha = Q_{\text{NH}_3}/Q_{\text{BF}_3}$ . The susceptor temperature was measured by mean of an optic pyrometer.



**Fig. 1.** Apparatus used for continuous BN processing (schematics).

## *Characterisation*

After treatment, the samples were broken and the fracture surfaces of the BN deposits were observed with a scanning electron microscope (SEM) (HITACHI S800).

Structural measurements were performed by two complementary methods: X-ray diffraction (XRD: Philips PW 3710,  $\lambda_{\text{Cu}} = 0,15418$  nm) and Raman spectroscopy (Jobin-Yvon, Ramanor,  $\lambda = 514,5$  nm). In theory, coherent length  $L_c$  and  $L_a$  can be respectively deduced from the full width at half-maximum (FWHM) of the 002 ( $2\theta = 26.7^\circ$ ) and 100 ( $2\theta = 41.6^\circ$ ) diffraction bands by Scherrer equation:

$$L = \frac{k \lambda}{\text{FWHM} \cos \theta}$$

In practice, only the 002 band is intense and well-defined enough for this calculation ( $k = 1.84$ ). The 100 band analysis is possible ( $k = 0.9$ ) but a deconvolution of the superimposed 100 and 101 bands is required. Raman spectroscopy allows a better estimation of the average graphitic plan length from the  $1367 \text{ cm}^{-1}$  band analysis. The FWHM of this band is proportional to  $1/L_a$  [7].

The chemical composition of the BN deposits was determined by X-ray photoelectron spectroscopy (XPS: Helwett-Packard 5950A) using a focused monochromatic Al  $K_\alpha$  radiation (1486.6 eV).

Tensile tests were performed at room temperature on coated fibres (separated at random from the treated tow) and uncoated fibres (as a reference) with an MTS-Adamel DY-22 machine (Ivry sur Seine, France) equipped with a 5 N load cell. The crosshead speed was 0.1 mm/min. In each case, a batch of about 50 monofilaments was tested with a 20 mm gauge

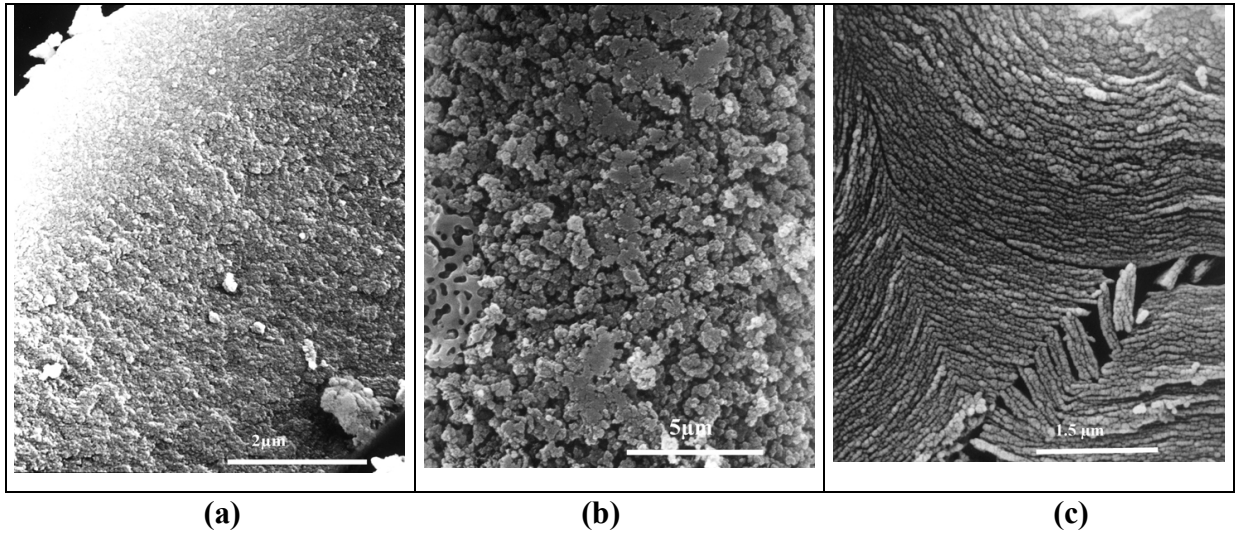
length. The characteristic fibre failure stress was determined by using the Weibull statistics with an associated probability of failure equal to 0.632 [8 - 9].

## **RESULTS AND DISCUSSION**

### *Static LPCVD-process study*

The influence of temperature, total pressure and initial gas phase composition  $\alpha$  was first studied without fibre displacement, using isothermal and isobar conditions. With these "static" treatments (about one hour duration), the coatings were thick enough to determine their morphology or apparent texture by mean of a simple SEM observation. As the temperature was not uniform along the whole susceptor length, the coated fibre was always extracted from the same place located in the hottest reactor area. This qualitative observation evidences the occurrence of three possible textures for the BN coatings. They are referred to as smooth isotropic ( $I_s$ ), rough isotropic ( $I_r$ ) and anisotropic (A). The texture  $I_s$  corresponds to a flat aspect of the fracture surface (Fig. 2a) while the  $I_r$  fracture surface seems to be rougher but still homogeneous and without preferential grain orientation or distribution (Fig. 2b). The BN coatings with texture A clearly exhibit a laminated fracture surface (Fig. 2c)

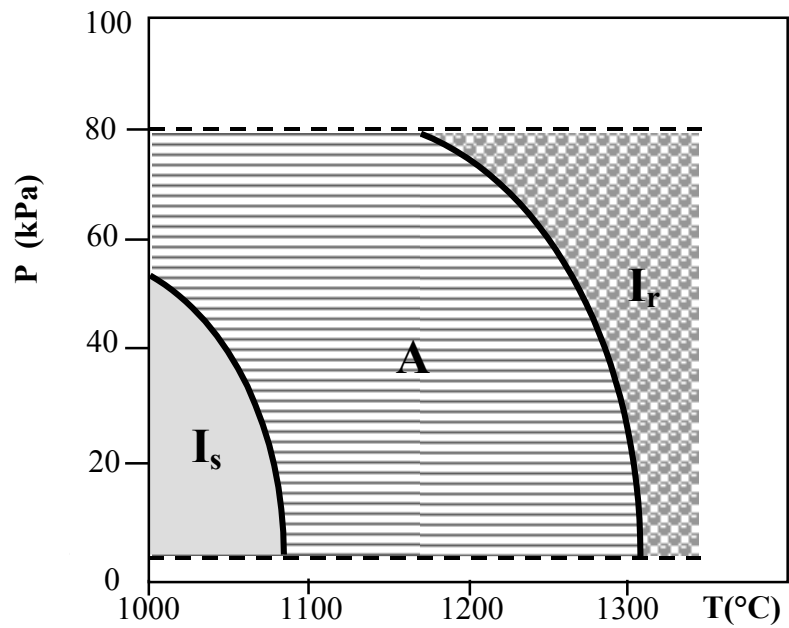
Obviously, the formation of each texture depends on the pressure, the temperature and the initial gas phase composition. Thanks to numerous experimental runs, texture diagrams could be established where each domain gives relationships between a given texture and CVD processing conditions. The transition from one texture domain to another is comparatively sharp.



**Fig. 2.** Different textures for the BN coatings  
 (a) smooth isotropic ( $I_s$ ), (b) rough isotropic ( $I_r$ ), (c) anisotropic (A)

*Influence of total pressure and temperature*

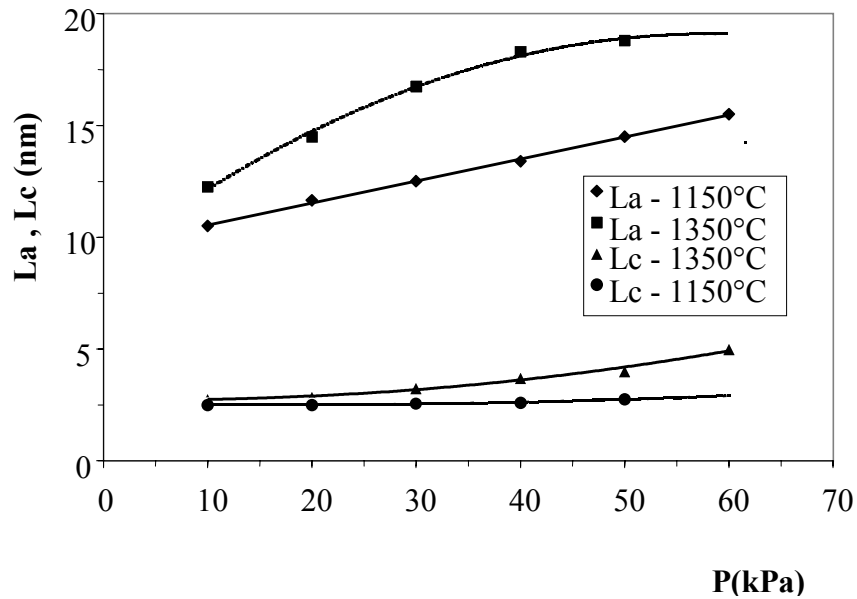
A first diagram is reported in figure 3 for  $\alpha = 2$ . Domain  $I_s$  is restricted to low temperature ( $< 1070^\circ\text{C}$ ) and low-pressure scale ( $< 50$  kPa). Domain A appears for intermediate temperatures and extends over a large range of pressure.



**Fig. 3.** Pressure versus temperature texture diagram ( $\alpha = 2$ ).

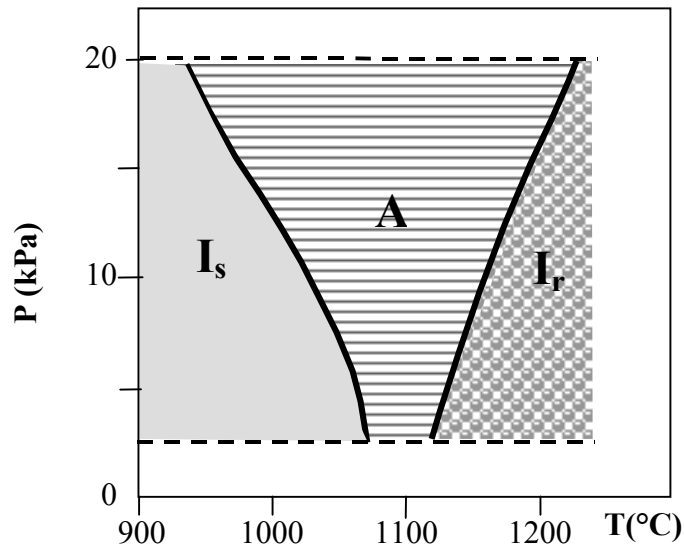


As a general rule, lamellas are more pronounced as the pressure increases. This feature is confirmed by XRD and Raman spectroscopy, which show an increase of the crystallite size with the pressure increasing (Fig. 4). Finally domain  $I_r$  appears at high temperature.



**Fig. 4.**  $L_a$  and  $L_c$  (XRD) versus pressure ( $\alpha = 0.5$ ,  $T = 1150^\circ\text{C}$  and  $1350^\circ\text{C}$ ).

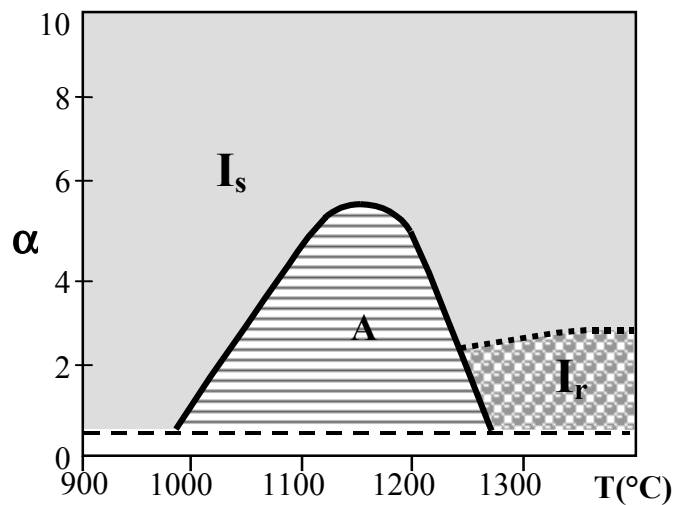
A second texture diagram is reported in figure 5 for  $\alpha = 0.5$ , i.e. for a higher  $\text{BF}_3$  content in the initial gas phase. In that case, domain A is very narrow at low pressure and widens out when pressure increases. For instance, the deposit is laminated for  $P = 5$  kPa and  $1050^\circ\text{C} < T < 1150^\circ\text{C}$  and for  $P = 20$  kPa and  $950^\circ\text{C} < T < 1250^\circ\text{C}$ . Thus, with  $P = 20$  kPa, which is a low enough pressure for a good infiltration of a fibre tow, an anisotropic BN coating can be obtained at almost any temperature. So, pressure was maintained at 20 kPa for the following study.



**Fig. 5.** Pressure versus temperature texture diagram ( $\alpha = 0.5$ ).

*Influence of  $\alpha$  composition and temperature*

This study was restricted at  $\alpha > 0.5$ . Below this limit, the gas is too much aggressive towards the Hi-Nicalon fibre. Figure 6 shows that domain A temperature range decreases when gas mixture becomes impoverished of  $\text{BF}_3$ . Thus, the coating is anisotropic for  $\alpha = 0.5$  and  $900^\circ\text{C} < T < 1300^\circ\text{C}$ , for  $\alpha = 2$  and  $1020^\circ\text{C} < T < 1250^\circ\text{C}$  and for  $\alpha = 5$  and  $1120^\circ\text{C} < T < 1200^\circ\text{C}$ . For  $\alpha > 6$ , only an isotropic deposit is observed at any temperature.



**Fig. 6**  $\alpha$  versus temperature texture diagram ( $P = 20$  kPa).

### *BN growth mechanism*

Quantitative XPS analyses revealed that every deposit is made of stoichiometric BN. The equivalence ratio B/N remains comparatively constant; it ranges from 0.98 for  $\alpha = 1$  to 1.02 for  $\alpha = 0.5$ . Thus, the different textures are not connected with composition variation. A  $\text{BF}_3$  rich mixture (low  $\alpha$ ) is favourable to an anisotropic BN processing. This feature can be explained by the trigonal planar geometry (with bond angles of  $120^\circ$ ) of  $\text{BF}_3$  molecule that foreshadows the  $\text{B}_3\text{N}_3$  hexagonal shape of boron nitride. On the contrary, the pyramidal shape of ammonia is detrimental to BN structural organisation. Consequently, the BN deposit becomes isotropic for high  $\alpha$  values.

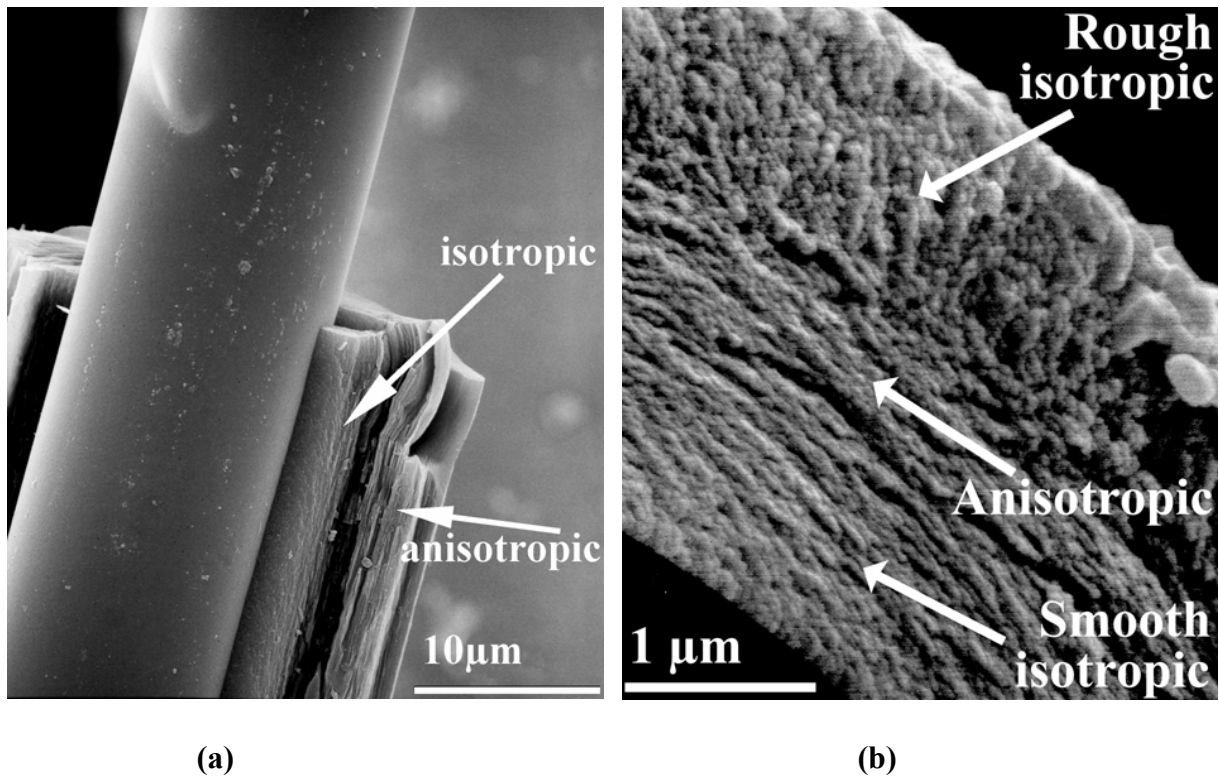
A previous kinetic study carried out by Prouhet *et. al* on CVD BN growth can explain the sharp transition from one texture to another [10]. The conditions of this work were similar to the present study. Prouhet *et. al* reported that BN growth rate is governed by different mechanisms depending on pressure and temperature processing. For a given pressure, below a pivot temperature, the BN growth is governed by a surface reaction mechanism, and above, it switches to a diffusion mechanism. From a comparison between both studies, it appears that the former mechanism at low temperature yields texture  $I_s$ , while the latter at higher temperature yields texture A. An interpretation of the third texture  $I_r$  obtained at high temperature ( $> 1200\text{-}1300^\circ\text{C}$ ) is more delicate. The deposit surface roughness (with sometimes outgrowths) could be explained by a homogeneous nucleation. Figure 7 illustrates a pronounced case.



**Fig. 7** Deposit processed with homogeneous nucleation ( $T > 1300^{\circ}\text{C}$ )

#### *Transient mechanism treatment*

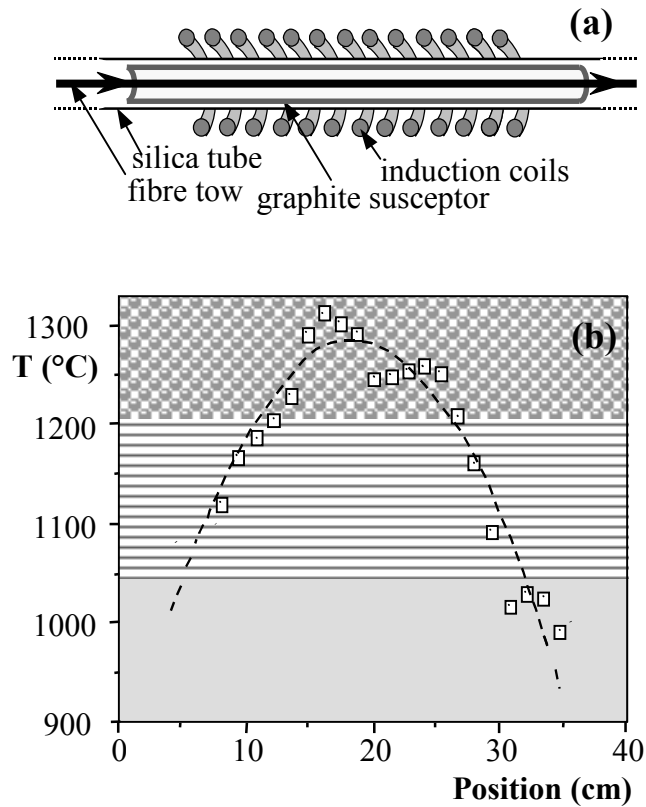
Texture diagrams reveal that a slight variation of one CVD-process parameter ( $\alpha$ , T or P) can result in a deposit texture transition. This feature was first illustrated with an experiment in which the pressure have been continuously increased from 0 to 20 kPa during 40 minutes and then maintained constant during 30 minutes at  $1200^{\circ}\text{C}$  with  $\alpha = 0.5$ . SEM observation of the deposit (Fig. 8.a) shows that it is made of two layers: the first one near the fibre is isotropic  $I_s$  and corresponds to low pressures, the second one is clearly anisotropic with lamella orientated parallel to the fibre surface. A second experiment was carried out at 20 kPa with  $\alpha = 0.5$  and temperature increasing continuously from  $950^{\circ}\text{C}$  to  $1300^{\circ}\text{C}$ . SEM observation confirms the occurrence of a first isotropic layer  $I_s$ , followed by a second anisotropic layer A and a third rough layer  $I_r$  (Fig. 8.b)



**Fig. 8** Multilayered coating - with increasing pressure (a)  
 - with increasing temperature (b)

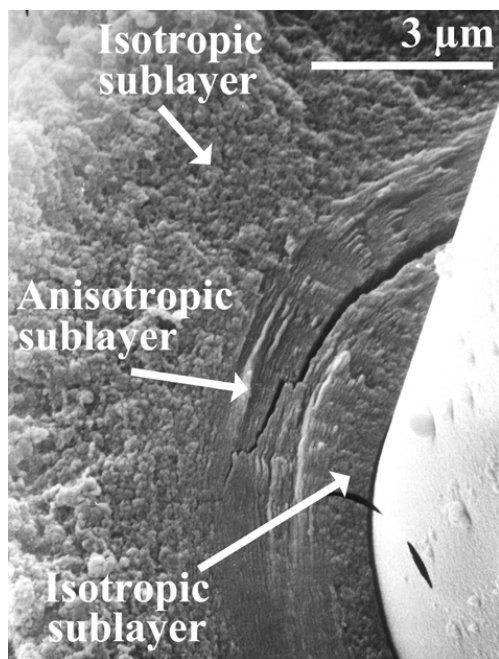
*Continuous dynamic LPCVD-process study*

The aim of the present study was to perform a continuous dynamic treatment, i.e. with a fibre tow displacement through the susceptor. During such a treatment,  $\alpha$  and  $P$  remain constant but the fibre undergoes a temperature profile while travelling: the temperature continuously increases from a “cold” area at the entrance to a hot area at the centre ( $T_{\max}$ ) and finally decreases at the outlet of the susceptor. The temperature profile measured along the susceptor is given figure 9.



**Fig. 9.** Schematics of the reactor (a) and temperature profile (b) measured along the susceptor (---□---).

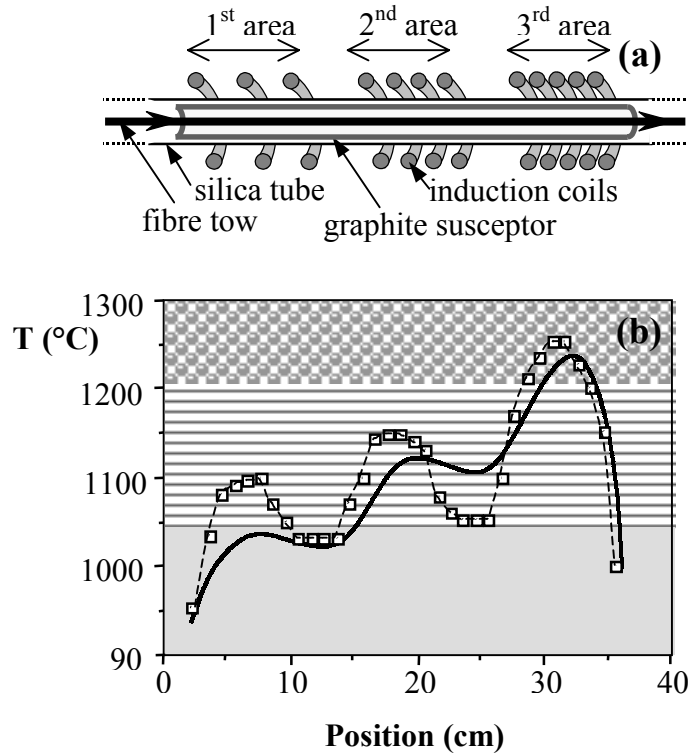
With  $\alpha = 2$  and  $P = 20$  kPa, according to texture diagrams, the BN coating should be made of five sublayers with the following expected theoretical sequence:  $I_s/A/I_r/A/I_s$ . By using a low displacement rate ( $r = 0.5$  m.h<sup>-1</sup>), we can observe that the experimental coating is made of only 3 sublayers (Fig. 10)  $I_s/A/I_r$ . The absence of the last two sublayers can be due to a sharp decrease of the reactive gaseous species content at the outlet of the reactor.



**Fig. 10.** BN coating with 3 sublayers ( $P = 20$  kPa,  $T_{\max} = 1300^{\circ}\text{C}$ ,  $\alpha = 2$ )

With high displacement rates ( $r \geq 3$  m.h<sup>-1</sup>), the BN deposits are thinner ( $< 0.5$   $\mu\text{m}$ ) and difficult to observe by SEM. Such thicknesses are compatible with interphases of CMCs but in these conditions the coated fibre failure stresses are significantly lowered ( $\sigma_F < 2000$  MPa) compared with the initial value of the non-treated Hi-Nicalon fibre ( $\sigma_F \approx 3000$  MPa). This feature evidences that the SiC fibre does not stay a long time enough in the low temperature area and consequently a first isotropic layer cannot protect it.

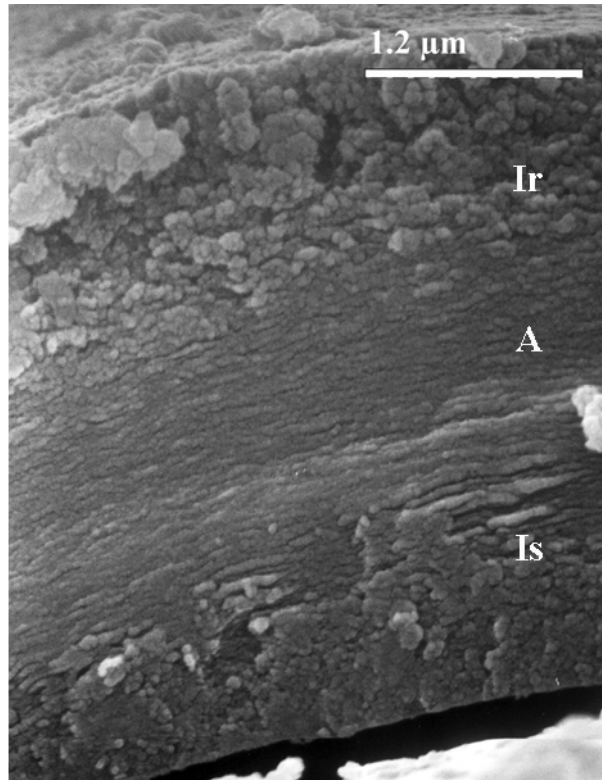
In order to overcome this phenomenon, the initial susceptor temperature profile was modified: the total “cold” temperature area is increased thanks to a variable pitch of induction heating coil turns (Fig. 11). Thus, the reactor contained three distinct hot areas with respectively a "low" temperature ( $< 1100^{\circ}\text{C}$ ), a medium maximum temperature ( $\sim 1150^{\circ}\text{C}$ ) and a high one ( $\sim 1250^{\circ}\text{C}$ ).



**Fig. 11** Schematics of the susceptor with modified induction heating (a) and temperature profile (b) measured along the susceptor (-□-) and actually followed by the fibre tow at  $r = 0.5 \text{ m.h}^{-1}$  (—).

The idea was to favour the isotropic coating growth that protects the fibre before aggressive coating conditions. Such a temperature profile should promote pronounced transitions between each sublayer. At the outcome of the susceptor, the temperature gradient is very high and consequently, the rapid resulting cooling should prevent an external  $I_s$  layer formation. Hence, the last sublayer obtained in the hottest area should be rough ( $I_r$ ) and favourable to a good further adhesion of a SiC matrix. Still with  $\alpha = 2$  and  $P = 20 \text{ kPa}$ , if the fibre tow follows exactly the measured temperature profile, the expected BN coating should contain the following sequence of sublayers:  $I_s/A/I_s/A/I_r$ . Actually, with  $r = 0.5 \text{ m.h}^{-1}$  the third expected sublayer  $I_s$  is not observed (Fig 12).





**Fig. 12.** BN coating with 3 sublayers

This discrepancy is certainly due to a different temperature profile followed by the fibre tow: because of the displacement, fibre heating and cooling are slightly delayed along the susceptor (Fig 11). It is worth noting that the growth rate of BN depends on temperature and consequently, sublayer thickness does not proportionally correspond to texture domain lengths shown by the schematics.

With high displacement rate ( $r = 3 \text{ m.h}^{-1}$ ), the total BN deposit thickness is about  $0.8 \mu\text{m}$  and tensile tests do not evidence a significant decrease of the fibre failure stress. The study of such BN coatings as interphases in SiC/SiC composites is reported elsewhere [11].

## CONCLUSION

Thin BN layers with a lamellar structure could be deposited from  $\text{BF}_3$  and  $\text{NH}_3$  gaseous species onto fibres that were travelling continuously inside a LPCVD reactor. The structural anisotropy can be obtained at 20 kPa above 1200°C. These conditions are aggressive towards the fibre. Nevertheless, the occurrence of a temperature gradient along the susceptor heated by induction enables to process in one step a multilayered coating with different textures. If the first cold area located at the entrance of the susceptor is extended enough, the first BN sublayer is isotropic and protects the Hi-Nicalon fibre from the aggressive gaseous mixture at high temperature. In these conditions, the mechanical properties of the treated and non-treated fibres are similar. The use of such BN thin coatings as interphases in ceramic matrix composites can be considered.

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