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OXIDATION RESISTANCE OF CVD BN COATINGS : CORRELATION WITH PROCESSING CONDITIONS

S. Le Gallet, F. Rebillat, A. Guette and R. Naslain,
Laboratoire des Composites Thermostructuraux, Pessac, France

SUMMARY : From the two different precursor gas systems, (BF_3-NH_3-Ar) and (BCl_3-NH_3-H_2), a wide range of BN coatings with increasing order have been deposited at low pressure and relatively low temperature on different substrates (fibre bundles or planar substrates). The isothermal oxidation of the coatings was carried out at 950°C in dry air. Different oxidation behaviours were observed depending on the microtexture of the coating, the quantity of crystallographic plane edges emerging from the surface and the precursor gas system.

KEYWORDS : BN, CVD, oxidation, precursor, microtexture

INTRODUCTION

It is now well acknowledged that properties of fibre/matrix interfaces determine the mechanical behaviour of brittle-matrix composites [1,2]. Non-linear deformations result from the deflection of matrix cracks into the fibre-matrix interfaces. This phenomenon can be controlled through the deposition of a layer of a soft material over the fibres. Boron nitride has been suggested as an alternative to anisotropic pyrocarbon in various ceramic matrix composites (CMCs) for service at elevated temperatures in oxidising atmospheres [3-5].
The chemical and physical properties of hexagonal boron nitride are improved as soon as its crystallisation degree is high, the structure becoming somewhat similar to that of graphite. Under such conditions, it can be used (instead of pyrocarbon) as an interphase in ceramic matrix composites.
Generally, BN layers display only a poor turbostratic texture under commonly used CVD/CVI conditions. Previously, it has been shown that it was possible to obtain thin coatings of Pyro-BN by low pressure chemical vapour deposition (LPCVD), from two different precursor gas mixtures, (BF_3-NH_3-Ar) or (BCl_3-NH_3-H_2), with a controlled microtexture in order to achieve a range of mechanical characteristics similar to that previously reported for pyrolytic carbon interphases [6].
The aim of this work was to correlate the oxidation resistance of thin coatings of Pyro-BN with the processing parameters in LPCVD, i.e. with the microtexture, and with the precursor gas mixtures chosen.

PROCESSING OF THE BN COATINGS

- ***Processing conditions***

A wide range of BN coatings with improving crystallinity (from isotropic to highly crystallised with a three-dimensional order) have been deposited at low pressure and relatively low temperature (LPCVD) from the two different precursor gas systems, (BF_3, NH_3, Ar) and (BCl_3, NH_3, H_2) [6,7]. The inlet composition of the gas phase was described, as a function of the gas flow rates (Q_{BX3} with X=F or Cl, Q_{NH3}, and Q_{Ar} or Q_{H2}), by the $\alpha = Q_{NH3}/Q_{BCl3}$, and $\beta = Q_{Ar}/(Q_{NH3}+Q_{BF3})$ or $\beta = Q_{H2}/(Q_{NH3}+Q_{BCl3})$ ratios. The coatings from the (BCl_3, NH_3, H_2) precursor gas system were processed at temperatures lower than for the (BF_3, NH_3, Ar) system [7]. The as-processed boron nitride coatings were found amorphous. Thus, for this system, a post-deposition heat treatment at a higher temperature but still compatible with the chemical stability of SiC fibres used as substrate, was therefore required to achieve crystallisation. XRD pattern (Fig. 1) confirms the crystallisation of the heat treated coating. A thin intense (002) diffraction peak is apparent on the XRD spectrum of the heat

treated BN whereas only a very broad band characterises the amorphous state of as-processed BN. The thermogravimetric analyses (Fig. 2) confirm the increase of the degree of crystallisation through the significant improvement of the oxidation resistance of the heat treated coatings.

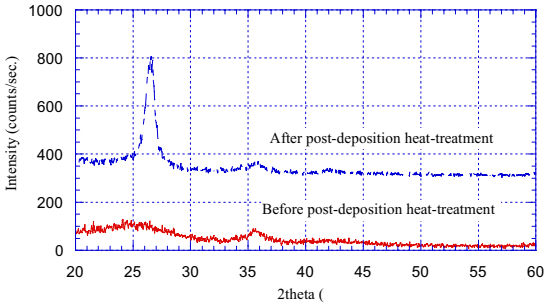

Fig. 1 XRD spectra of BN coatings from the (BCl_3, NH_3, H_2) system

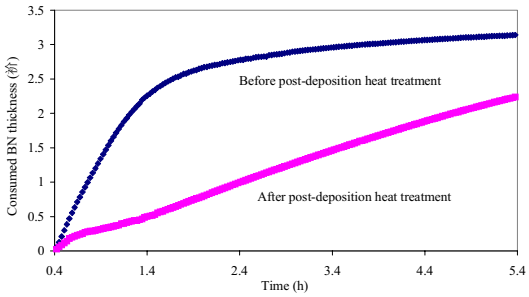

Fig. 2 TGA results of BN coatings from the (BCl_3, NH_3, H_2) system

Therefore, in the present study, the coatings processed from the (BCl_3, NH_3, H_2) system have been systematically heat-treated.

- ***Description of the coatings***

The Fig. 3-5 illustrate the crystallisation degree of BN CVD-coatings as a function of the processing parameters.

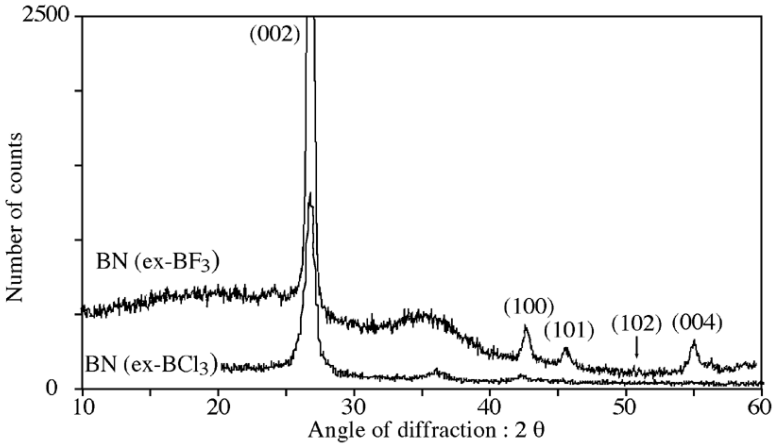

Fig. 3 XRD spectra of highly crystallised BN coatings deposited either from the (BF_3, NH_3, Ar) or the (BCl_3, NH_3, H_2) system

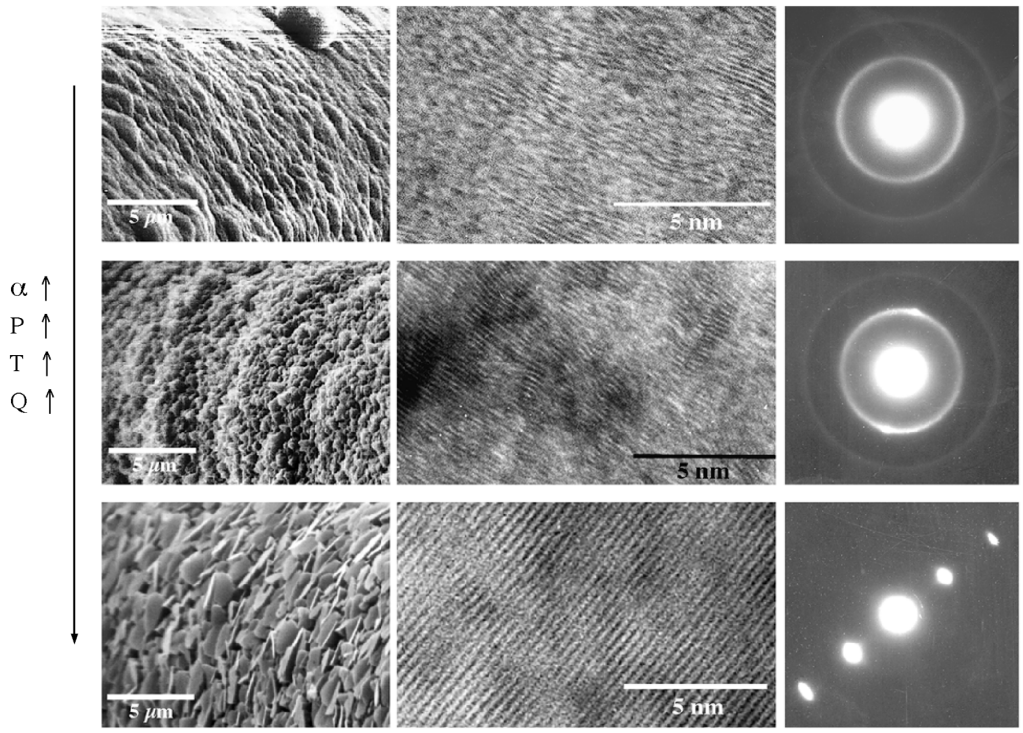

Fig. 4 Evolution of morphology and texture of BN coatings from the (BF_3, NH_3, Ar) system with α,P, T and Q

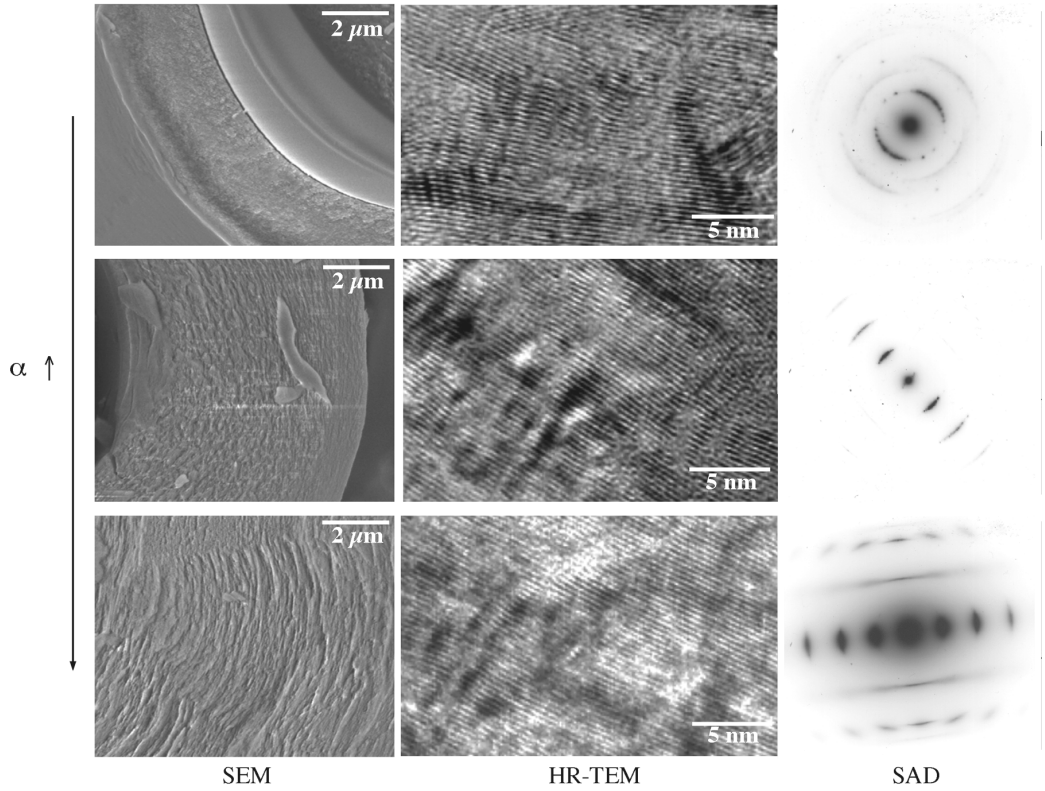

Fig. 5 Evolution of morphology and texture of BN coatings from the (BCl_3, NH_3, H_2) system with α

For the (BF_3, NH_3, Ar) system and for increasing values of processing parameters (T, P, α), the SEM observations of the coating surfaces show the occurrence of grains with sharper and sharper edges. The shape of the crystals reveals the gradual organisation of the BN coatings in the hexagonal structure. The highly crystallised BN grows with a columnar texture. Within each column, the (002) planes are parallel to each other and to the fibre surface. The corresponding inter-reticular distance (3.34 Å) is very close to the theoretical value (3.33 Å) and the width at mid-peak height (2θ) is also very narrow (0.38°).
For the (BCl_3, NH_3, H_2) system and for increasing values of the α parameter, the SEM observations of cross-sections of broken coatings reveal a progressive improvement of anisotropy through the presence of a layered structure. With an increase of the α parameter, the tablets forming the coating extend in the lateral direction, parallel to each other and to the fibre surface. With the extension of the tablets, an apparent continuous structure with (002) planes without visible limits which seems to embed nicely the fibres or the planar substrates appears. Their inter-reticular distances (between 3.37 and 3.39 Å) and widths at mid-peak height (between 0.8 and 1,1°) are higher than those of the most crystallised coating processed from the (BF_3, NH_3, Ar) system.
The main difference in the texture between the highly crystallised BN coatings, processed from different gas precursors, lies in the lateral extension of the (002) planes. The structure matches quasi-monocrystals for the BN processed from BF_3 whereas it is a quasi-continuous but slightly distorted structure all around the fibres for the BN processed from BCl_3.
In the present work, the BN CVD coatings were deposited on SiC Nicalon fibres (Nicalon NLM 202 or Hi-Nicalon from Nippon Carbon, Japan) and SiC flat substrates. The coatings are 0,9 to 2,8 µm thick for the (BF_3, NH_3, Ar) system, whereas they are 4 to 16,5 µm thick for the (BCl_3, NH_3, H_2) system (the deposition rates being higher).

EXPERIMENTAL PROCEDURE

The thermogravimetric analyses (TGA) were performed using a TAG 24 (SETARAM, France) equipped with a vertical alumina tube and a balance with a sensitivity of 1 µg. The atmosphere consisted of reconstituted dry air. The tests were performed at 950°C during 5 hours. Specimens were either fibre bundles or flat substrates coated with BN. The bundles were cut in 8 mm lengths and set horizontally in an adapted crucible. The flat substrates were not cut and set horizontally on four points allowing a uniform oxidation.
The oxidation resistance of the BN coatings has been compared with that of a commercial CVD BN also processed from the (BCl_3, NH_3, H_2) system, at a very high temperature (~ 2000°C), by Advanced Ceramics Corporation [8, 9]. This BN is highly crystallised with an inter-reticular distance of 3.33 Å but its width at mid-peak (0.8°) is the same as that of the coatings processed from the (BCl_3, NH_3, H_2) system in present work.
This BN is massive (5×2×1 mm) and 60% of its surface consists of plane edges whereas the other coatings on planar substrates did not present accessible plane edges. The amount of plane edges at the sections of the fibre bundles exposed to the air was estimated < 1% of the total surface.
After oxidation, the samples were observed by optical and scanning electron microscopies to evaluate the thickness of the remaining BN coating.

OXIDATION RESISTANCE OF THE COATINGS : RESULTS AND DISCUSSION

A B_2O_3 glass is formed on the surface of BN coating resulting from oxidation. Because of its low vapour pressure in dry air and below 1100°C [10], the B_2O_3 glass is thought to remain in a condensed state. Oxidation proceeds via diffusion of oxygen through the B_2O_3 layer, with a conversion rate depending on the oxygen partial pressure.

• ***Thickness of remaining BN coatings after oxidation***

The initial thicknesses of the coatings on the fibre bundles are very different. The mass variation per surface unit, Δm/S, is usually calculated to estimate the oxidation resistance of materials. For coatings on bundles, it is relatively difficult to determine accurately the initial surface of the coating. Moreover, for a cylindrical geometry, the sample surface varies with the oxidation time (as a function of the square of the radius). Thus, the results have been presented as the function *consumed BN thickness = f(time)*. The thickness of the consumed BN layer, as a function of time, has been calculated from the weight gain, by taking into account the quantity of produced B_2O_3 and the geometry of the sample. However, the expression of the consumed BN thickness depends on the initial BN thickness, which is not ideally homogenous within the bundle. The expressions of the average consumed BN thickness are :

- for planar substrates, $$X_{BN} = \frac{\Delta m}{S \cdot \rho_{BN}} \cdot \frac{2 \cdot M_{BN}}{M_{B2O3} - 2 \cdot M_{BN}} \quad (1)$$

- for bundles, $$X_{BN} = (r_f + X^0_{BN}) - \left[(r_f + X^0_{BN})^2 - \frac{\frac{\Delta m}{500 \cdot \pi \cdot L \cdot \rho_{BN}}}{\frac{M_{B2O3}}{2 \cdot M_{BN}} - 1} \right]^{1/2} \quad (2)$$

with X_{BN} the consumed BN thickness, X^0_{BN} the initial BN thickness, r_f the fibre radius, L the bundle length, S the planar substrate area and Δm the overall mass variation.

• ***TGA measurements***

BN coatings from the (BCl_3, NH_3, H_2) system

The tests on different shapes of samples with different degrees of crystallisation of BN indicate how the oxidation behaviour is dependent on structure and texture.

- Coated bundles (Fig. 6)

The lower oxidation rate observed after few hours can be related to the growth of the glassy phase covering the BN layer and therefore limiting further oxidation. The TGA curves are indeed parabolic, suggesting that oxidation is limited by the oxygen diffusion through the oxide layer. However, with such a geometry of sample, the glassy phase tends to flow. The parabolic kinetics constants could not be calculated and only the relative positions of the curves have been compared.

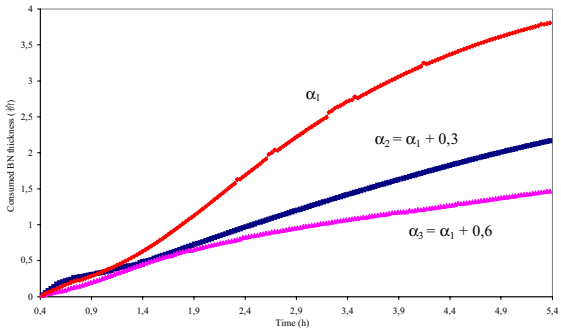

Fig. 6 TGA curves of BN coatings on bundles from the (BCl_3, NH_3, H_2) system versus α ratio

- Coated flat samples (Fig. 7)

The TGA curves show a plateau at the beginning of the test with almost no weight gain. The duration of the plateau depends on the α parameter. At the end of the plateau, when the oxidation starts, the TGA curves become linear, suggesting an oxidation regime limited by surface reactions instead of oxygen diffusion through the oxide layer. The important calculated consumed BN layer (eq.1) suggests that the thickness of the boron oxide layer

should be at least as important and so this layer should slow down the oxidation rate. The observation of oxide drops on the bottom of the sample reveals the flowing of the boron oxide. Hence, on the bottom side, the layer of boron oxide is not uniform and does not seem to protect correctly the BN. In few places of the sample, the BN coating would be directly in contact with oxygen.

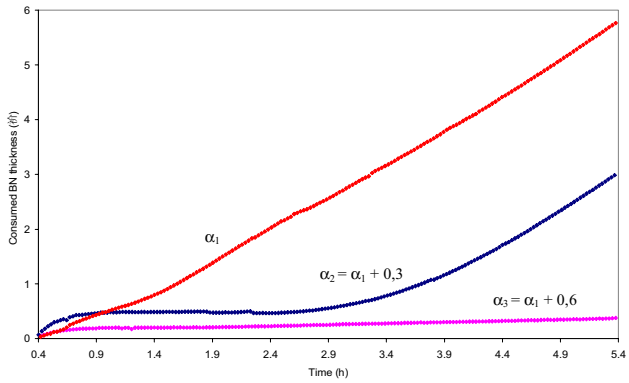

Fig. 7 TGA curves of BN coatings on planar substrate from the (BCl_3, NH_3, H_2) system versus α ratio

- Observations of the coatings

The optical or scanning electron microscopy observations of the coatings on the fibre bundles after oxidation did not allow a correct evaluation of the remaining BN thickness. Therefore, it is difficult to corroborate the thickness of consumed BN on bundles, as calculated from the TGA curves, with the experimental value measured through microscopy observations. However, some trends can be observed. For the BN coatings on planar substrates, the consumed BN thickness could be evaluated by optical microscopy from the initial thickness. The experimental measurements are in agreement with the values calculated from the TGA data.

- Comparison between the coated bundles and flat substrates and relation with the BN microtexture

The ranking in the oxidation resistance of the various BN microtextures remains the same whatever the substrate (bundles or planar substrates). However, different oxidation behaviours can be noticed depending on the substrates. Indeed, for the coatings on flat substrates, the TGA curves show an initial plateau which can be considered as an oxidation initiation delay, i.e., a latent time necessary to activate reactive sites. For such a layered material, the reactive sites can be assigned to the unbonded atoms at the edges of the (002) crystallographic planes. The BN plane edges of the coating, at the cut-ends of the fibre bundle samples, are directly in contact with oxygen. Then oxygen diffusion paths between the BN planes or at the BN/fibre interface are largely opened whereas such flaws do not exist for the coatings on planar substrates. After 5 hours, the consumed BN layer is thicker for the coatings on planar substrates than for the fibre bundle coatings, except for the BN deposited with the α_3 ratio. Although the B_2O_3 glass layer flows for both sample geometries, the BN might be better protected in the fibre bundles, at least, within the core of the bundle.

The thermogravimetric analyses of the coatings from the (BCl_3, NH_3, H_2) system generally show an improvement of the oxidation resistance with an increase of the α ratio. Since the BN coatings from the α_2 and α_3 ratios have very similar textures (Fig. 8, similar orientation of the (002) planes parallel to the substrate), the differences in their oxidation behaviour (variable length of the plateau on the oxidation curve) can be assigned to the coherent domain size (La).

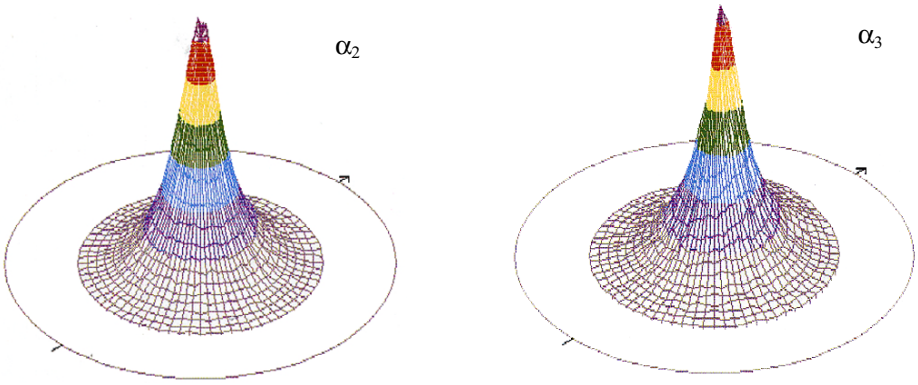

Fig. 8 XRD pole figures from the (002) planes of highly crystallised BN coatings processed from the (BCl_3, NH_3, H_2) system and for different α ratios

- Comparison with a commercial BN (Fig. 9)

The TGA curve of the commercial BN shows a parabolic behaviour similar to those of the coated bundles. Although better crystallised, the commercial BN is apparently less resistant against oxidation than the BN coatings deposited by CVD with the α_2 and α_3 ratios. Because of the sample geometries (different proportions of plane edges emerging from the surface and exposed to the air), the oxidation resistance of the commercial BN cannot be directly compared to those of the coated bundles or planar samples. However, its oxidation rate is indeed lower than those of flat BN coatings, once the oxidation is activated. The texture of the BN seems here to be at least as important as the presence of emerging plane edges on the oxidation rate.

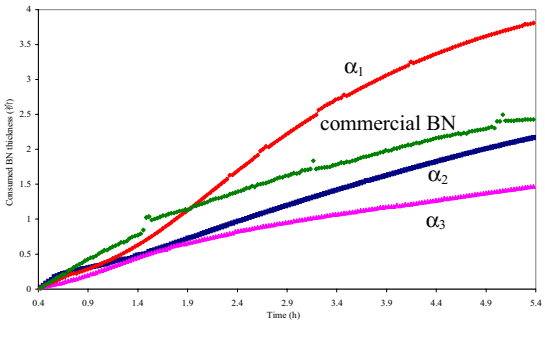

Fig. 9a) TGA curves of commercial BN and BN coatings on bundles from the (BCl_3, NH_3, H_2) system

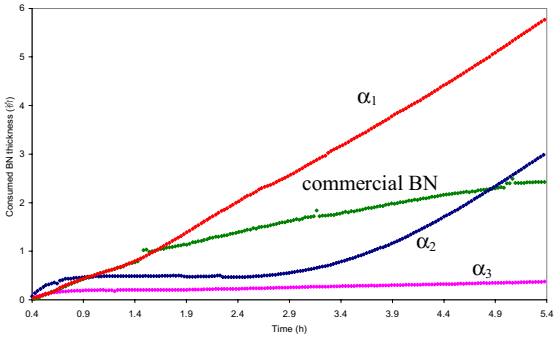

Fig. 9b) TGA curves of commercial BN and BN coatings on flat substrates from the (BCl_3, NH_3, H_2) system

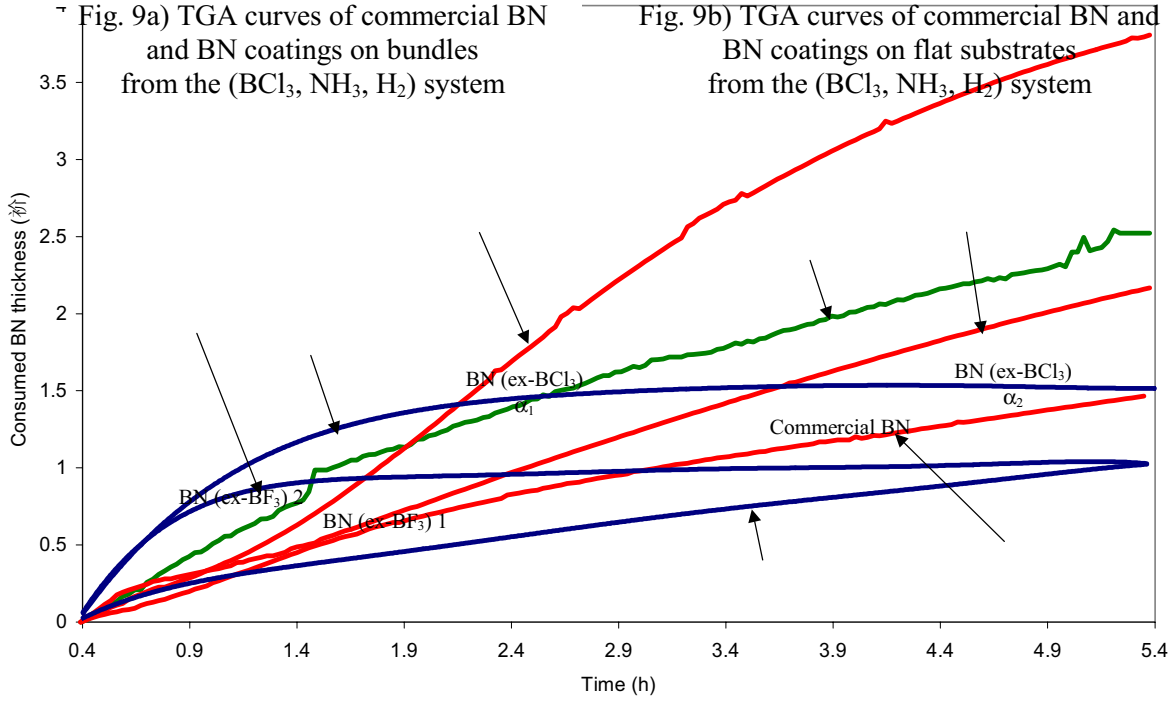

Fig. 10 TGA curves of commercial BN and BN coatings deposited on bundles either from the (BF_3, NH_3, Ar) or the (BCl_3, NH_3, H_2) system

Comparison of the oxidation resistance of BN coatings from various precursors

The highly crystallised BN coating (BN 3) from the (BF_3, NH_3, Ar) system displays a higher oxidation resistance than the highly crystallised BN coating from the (BCl_3, NH_3, H_2) system processed by CVD for CVI standard conditions.

Its oxidation resistance is even better than that of the commercial BN prepared by CVD in conditions incompatible with CVI (high temperature and deposition rate, leading to crystallised BN).

These remarks show the importance of the microtexture and mainly the lateral expansion of coherent domains which is determined by the processing conditions. Indeed, for these two gas precursors, the deposition mechanisms, although similarly described in the literature [11, 12], lead to different stackings of the (002) planes. The lower oxidation resistance of the BN processed from BCl_3 is probably related to a higher density of defects within the stacking of the (002) planes.

CONCLUSION

These experimental results demonstrate that in contrast with carbon, BN does not rapidly oxidise at a temperature of 950°C. They suggest that BN is a viable alternative to carbon. However a good control of the CVD processing conditions, from different precursor gas mixtures is required to produce a BN with a crystallographic structure close to that of the theoretical hexagonal BN. These results are in agreement with works that have been, for the moment, mainly performed on BN powders. Such textured BN can now be seriously considered as interphase material in SiC/SiC composites.

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