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Deposition and characterization of hex-BN coating on carbon fibres using tris(dimethylamino)borane precursor

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Abstract

Boron nitride thin films were deposited on carbon fibres by chemical vapor deposition from the single source precursor tris(dimethylamino)borane (TDMAB). Hydrogen was used as carrier gas and additional nitrogen was supplied in the form of ammonia. The heating of the substrate was performed by Joule effect. Detailed TEM structural and chemical analyses reveal a meso-graphitic structure with a stoichiometric B/N ratio as confirmed by Auger Electron Spectroscopy (AES). A penetration of carbon element from the fibre was observed in the BN layer close to the interface.

Keywords: TDMAB; Electron microscopy

1. Introduction

Hexagonal boron nitride (hex-BN) has recently received considerable attention due to its remarkable properties such as electrical resistivity, high thermal conductivity and chemical inertness. One of the most significant applications is the use of chemical vapour deposition (CVD) boron nitride as interfacial compliant material in thermostructural ceramic matrix composites.[1–3] At moderate temperature (700 °C), the presence of a thin hex-BN film between the fibres and the matrix instead of pyrolytic carbon improves the oxidation resistance in SiC-based composite systems. A barrier against oxidation by formation of B_2O_3 provides a better protection for fibres with the consequence to maintain the integrity of the composites for a longer duration under loading.[3]

The growth of hexagonal boron nitride thin film by CVD process is usually carried out using the reaction of borontrihalides such as BCl_3 or BF_3 with ammonia in excess relative to the boron source. However, although this process results in the improvement of the interfacial properties of the composites, hex-BN is expected to be poorly organized and isotropic with the use of BCl_3–NH_3 gaseous system. In the case of BF_3, it is required to protect the fibres from a chemical gaseous attack. An alternative to these conventional depositions is given by the organoboron precursors such as tris(dimethylamino)borane (TDMAB).[4,5] This single source precursor, liquid to the room temperature, contains both boron and nitrogen in the same molecule. Furthermore, it is non-toxic, non-explosive and non-corrosive for fibres or CVD device.

In this work, the feasibility of a deposition of hex-BN thin coating on carbon fibres by low pressure CVD in TDMAB/NH_3/H_2 gaseous system is reported. Chemical composition homogeneity of the coatings as well as detailed textural and structural aspects were also studied.

2. Experimental procedure

2.1. Processing

BN films were deposited on XN05 fibres (isotropic ex-brai carbon fibres produced by Nippon Graphite Fiber, average

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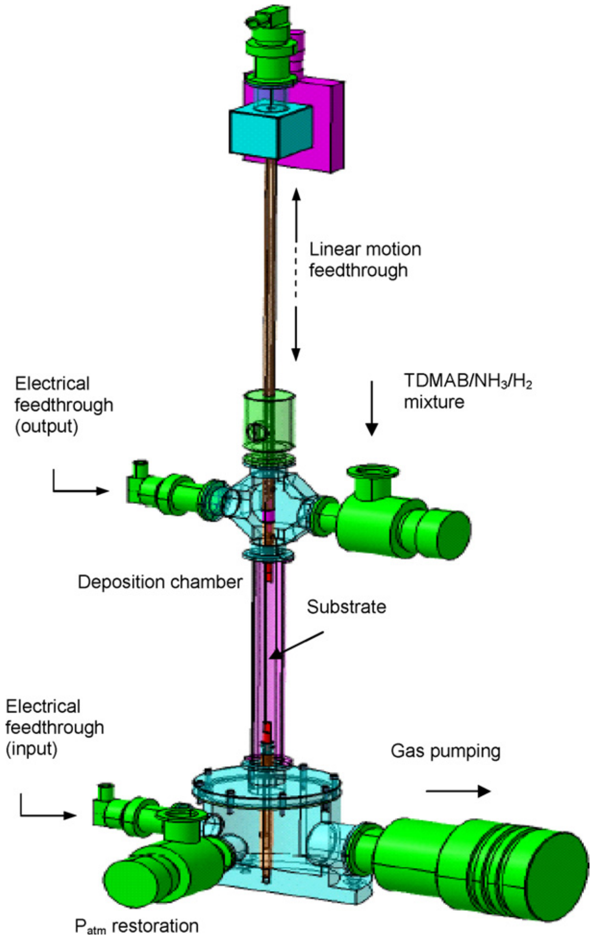

Fig. 1. CVD apparatus for BN processing (schematic)—heating by electrical energy dispelling into the substrate (Joule effect).

diameter 10 μm). They were partly chosen for their good mechanical resistance to high temperature. The precursor was a commercially available TDMAB (Aldrich Chemical, 99%) mixed with hydrogen that was used as a carrier gas. Processing conditions came from a previous study.[6] After flow rate regulation at 15 sccm, hydrogen was passed through a bubbler containing the liquid organoboron precursor maintained at a constant temperature of 35 °C. TDMAB enriched carrier gas was introduced in the vertical quartz chamber of the CVD apparatus (Fig. 1). Ammonia was added to the gaseous system with a nominal flow rate of 100 sccm in order to enhance nitrogen source. According to Rohr et al.[4] use of additional nitrogen source is necessary to obtain stoichiometric BN films and to reduce carbon contamination in the coating. All these gases were delivered through a low pressure gas network (0.3 bar), made up of stainless steel surrounded with heating wire to prevent possible re-condensation of the precursor.

One of the main particularities of the CVD process described in this work is given by the heating of the substrate. Contrary to the classical processes that use a hot wall furnace with a graphite susceptor, the heating was here ensured by the crossing of a current directly through the fibres. This heating by Joule Effect was possible due to the high electrical conductivity of the XN05 carbon fibres[7] (Fig. 2). The temperature was monitored by an optical bi-chromatic pyrometer and fixed at 1300 °C.

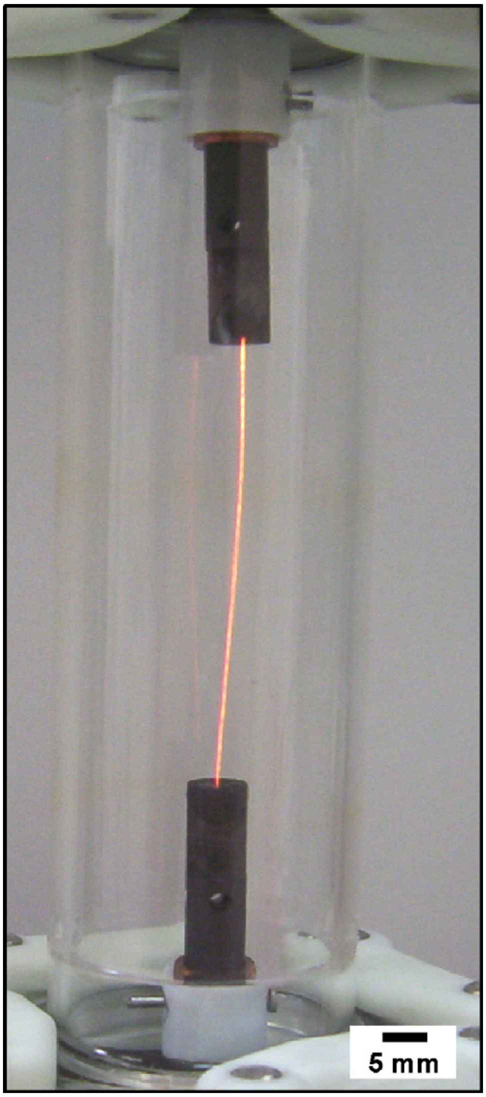

Fig. 2. Low pressure deposit chamber with a carbon fibre heated at 1300 °C.

2.2. Characterization

2.2.1. Chemical composition and microstructure

The BN chemical composition of the deposits was quantified by Auger Electron Spectroscopy (AES, VG microlab 310 F) coupled with argon-ion etching. The analysis of the respective atomic percentage of each element (B, C, N and O) was performed in depth profile after film etching with Ar^+ for 6 min to remove contaminants from the surface. AES surface scans carried out on longitudinal sections of samples were reported as well to closely observe the composition at the BN/fibre interface.

Texture and structure of the deposits were examined by transmission electron microscopy (TEM) including bright and dark field (BF, DF) modes, selected area electron diffraction (SAED) and high-resolution (HR) mode. To ensure a correct accuracy, TEM magnification has been calibrated using a gold standard

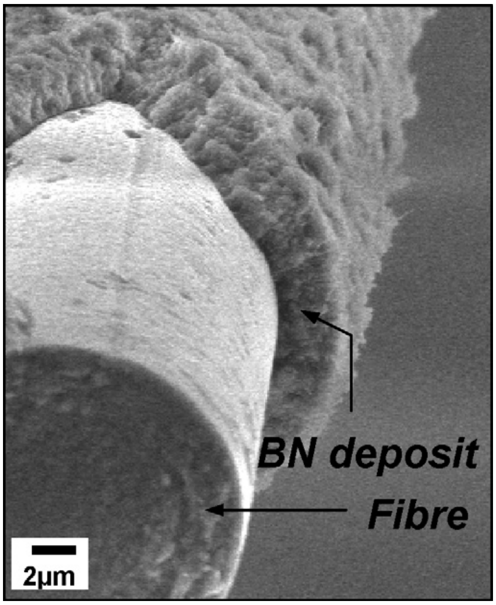

Fig. 3. SEM observation of the BN film obtained after 80 min deposition.

(S135 from Agar Scientific) with a *d*(2 0 0) spacing equal to 0.204 nm. Investigations were made with a Philips CM30ST microscope operating at 300 kV and equipped with a Gatan 666 Peels spectrometer. The results of analytical electron energy loss spectroscopy (EELS) in the energy range of 0–600 eV were compared with those of AES. GATAN EL/P program was used for this quantitative analysis. Analyses were performed on a sample batch obtained after 80 min deposition.

2.2.2. *Sample preparation for TEM analyses*

BN-coated fibres were thinned prior to the TEM observation using the method described by Berger and Bunsell.[8] A mesh of fibres impregnated with an epoxy resin was stuck on a 3 mm external diameter copper ring. Adjustment of fibres was carried out using an optical microscope so that fibres were perfectly aligned in contact with each other. The as-prepared sample was then directly ion milled with a Gatan Dual ion mill (Model 600). A beam of Ar^+ sputtered the centre of the sample at an incidence angle of 15° up to obtain a large region for observation.

3. Results and discussion

3.1. *SEM observation and growth kinetic*

A scanning electron microscopy observation (SEM, Hitachi S4500 FEG) of the BN film produced under the processing conditions mentioned above in 80 min is shown in Fig. 3. The carbon fibres are seen to be perfectly surrounded by the BN deposit. For short treatment times, low magnified image reveals a smooth surface of the thin deposit with very small grain sizes. Further growth of the BN layer results in a rather rough surface but without preferential grain orientation or distribution. Absence of flaws such as voids at the fibre/BN interface evidences a correct bonding.

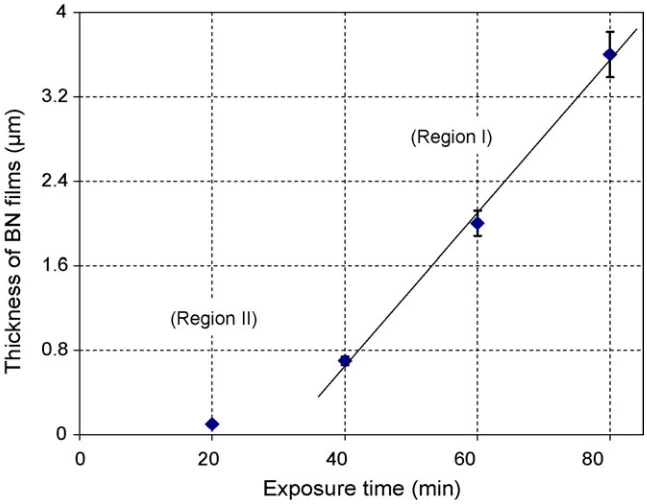

Fig. 4. BN growth kinetics in TDMAB/NH_3/H_2 gaseous system—variation of the thickness of BN film with exposure time.

The thickness of the BN film deposited on the carbon fibre is shown as a function of time in Fig. 4. For deposition times longer 40 min, thickness of the BN film increases linearly with time (region I). Typically, one hour of treatment is sufficient to reach a thickness of about 2 μm. For times shorter than 30 min (region II), the process seems to require initial delay time before reaching the stable regime. This result is consistent with the fact that NH_3 is known at high temperatures and low pressures to slowly react with the free carbon to produce a mixture of HCN and CH_4.[9]

Lastly, SEM cross-section observations of the BN deposited sample show a slight thickness gradient of the deposits all along the fibres (55 mm) taken into account by the error bars on the graph (Fig. 4) (<5%). That is linked to the thermal gradient induced by the heat process during the experiment (about 25 °C).

3.2. *AES examination*

AES depth profile analyses were performed through the BN deposits obtained at the end of different time exposures. Auger spectra were drawn up following the carbon, oxygen, nitrogen and boron elements. For the different examinations, the results are similar to each other. The B/N atomic concentration ratio has been found close to one within the deposits indicating a correct processing condition choice. The slight deficit in nitrogen as suggested by the presented spectrum (Fig. 5a) for which deposition time was 40 min may come from preferential etching. The high carbon content present in the inner regions of the deposit due to the pollution decreases drastically as soon as the outer surface of the BN layer is reached. It is however present within the granular BN layer for a few nanometres. Oxygen is only present as trace in the whole coating.

As for the BN/fibre interface, the analysed areas do not reveal oxygen excess but show an undeniable penetration of the carbon within the BN deposit. AES surface line scans carried out on a sample prepared for the TEM analyses across the interface report the observation (Fig. 5b). On this spectrum, the interface is represented by the vertical interrupted line.

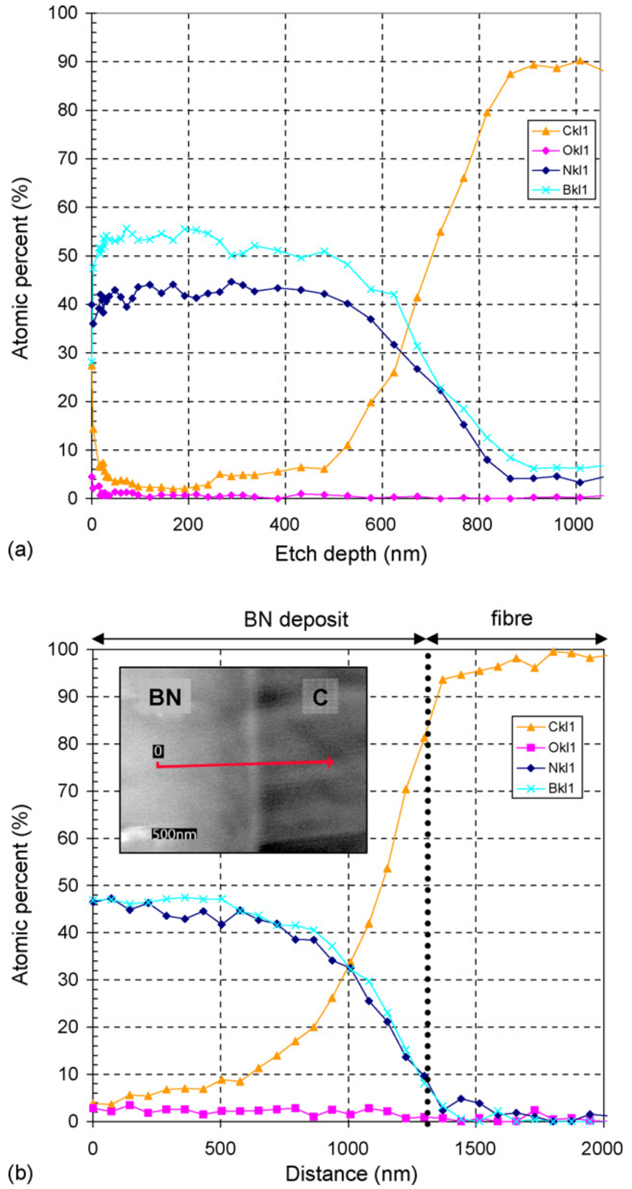

Fig. 5. (a) AES depth profile analyses through the BN film deposited on 40 min and (b) AES surface scan on the BN/fibre interface (sputter speed: 0.2 nm/s, SiO_2).

The contamination may be attributed to the parasite reaction observed at the start of deposit between ammonia and substrate. The exclusive high content carbon at the BN/fibre interface refutes a possible origin from the TDMAB precursor.

3.3. TEM analyses

3.3.1. General overview

The low magnification BF images, an example of which is given in Fig. 6, exhibit a wide distribution of crystallites. They appear bent and randomly oriented with various sizes ranging from one to a hundred nanometres. The large particles stay nevertheless relatively scarce. The BN coating morphology is described as a «fibrous morphology». Most of the grains have a needle-like shape while being entangled with each other. Except for some agglomerates of crystallites, the layer seems homogeneous in its thickness.

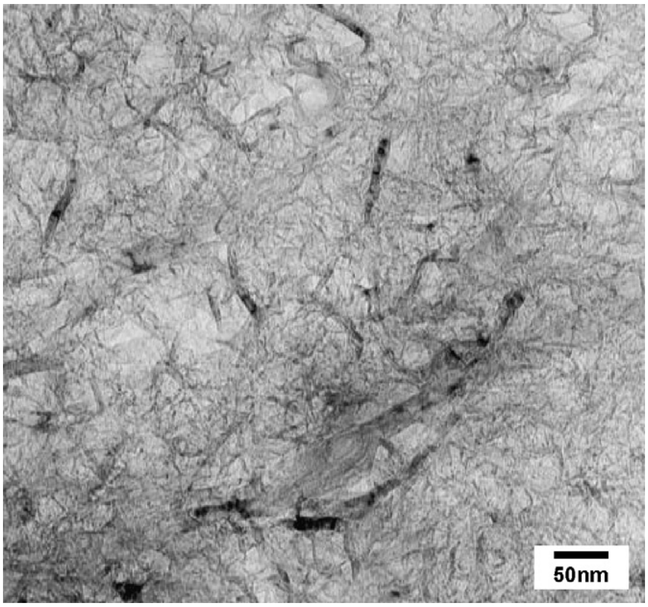

Fig. 6. BN coating BF micrograph (image).

The SAED patterns (Fig. 7) performed on the BN-coating show the (0 0 0 2) and (0 0 0 4) typical rings of the hexagonal BN structure. The (1 0 $\bar{1}$ 0) and (1 0 $\bar{1}$ 1) rings cannot be distinguished. The same holds for the (1 1 $\bar{2}$ 0) and (1 1 $\bar{2}$ 2) rings. They are, respectively, indexed 10 and 11 bands. From the diameter of the diffraction ring, lattice spacing associated with the (0 0 0 2) crystal plan is deduced to be equal to 0.35 nm.

Furthermore, as evidenced by the circular and continuous diffraction rings, an absence of texture is clearly observed in the deposit.

Fig. 8 shows DF observations of the same area on two parts of the selected (0 0 0 2) ring located at 90° from each other. In both cases, the crystallites having the (0 0 0 2) planes oriented in the Bragg conditions are numerous; it can be inferred from the shape and the orientation of the crystallites that there is an orientation relationship between the longitudinal axis of the crystallites and

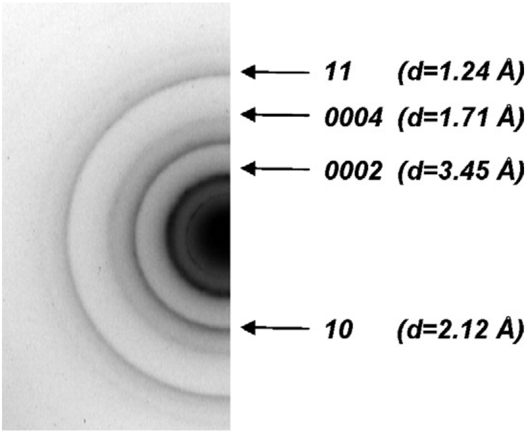

Fig. 7. SAED pattern of the h-BN coating obtained on 0.8 μm selected area, *d*-spacings are given in brackets.

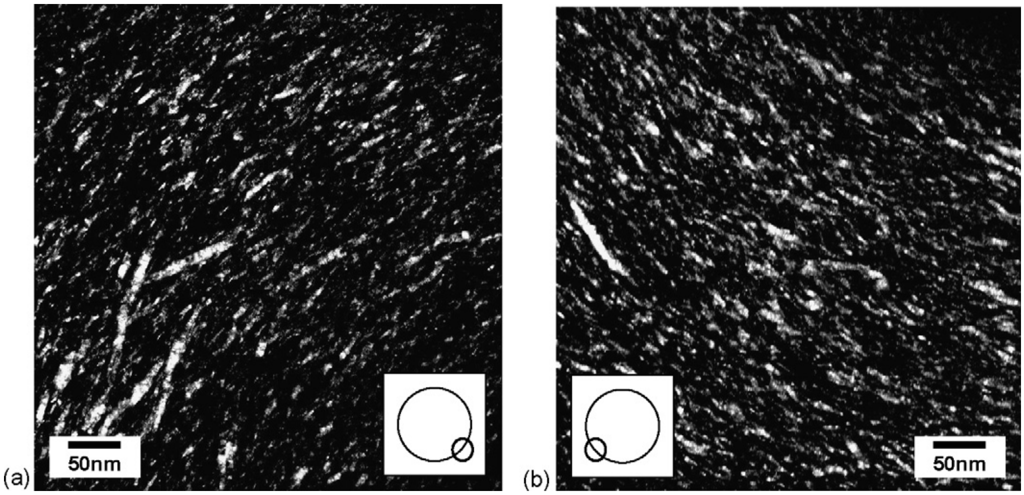

Fig. 8. (a) (0 0 0 2) DF image of the BN coating and (b) (0 0 0 2) DF image of exactly the same area after a 90° rotation of the SAED pattern. The BN deposit/fibre interface is located in the upper right corner of both images.

the (0 0 0 2) planes. At the same time, a study based on image processing gives both size and shape valuation of the present crystallites. The mean width and length are, respectively, equal about 6 and 13 nm.

3.3.2. High resolution

The high resolution TEM image of the longitudinal section of the deposit confirms that it is composed of elongated h-BN crystallites whose long axis is parallel to the (0 0 0 2) plane. The observed lattice fringes are characteristic of a good crystallisation degree (Fig. 9). They are however curved toward random direction displaying a certain isotropy.

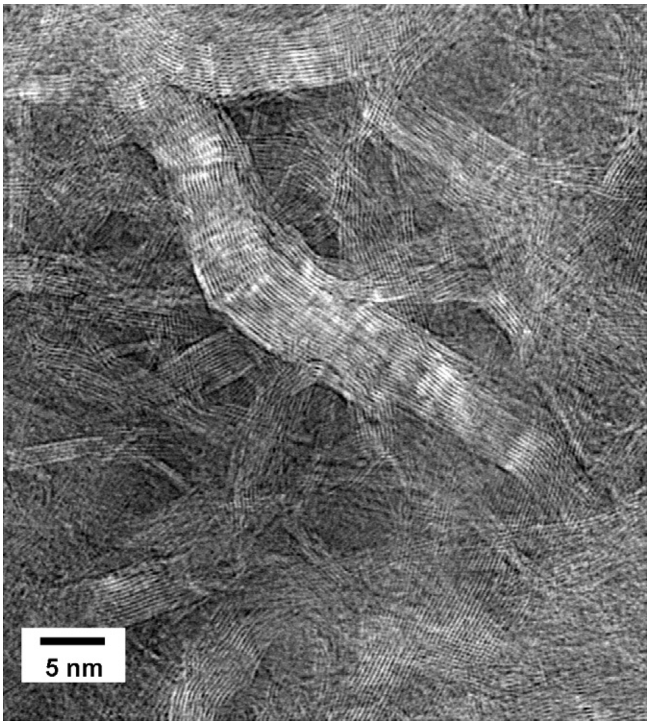

Fig. 9. HR-TEM image of a longitudinal section of the BN coating.

The degree of order in the hexagonal BN lattice is determined by measuring the lattice interlayer spacing. In that way, *d*(0 0 0 2) spacing has been measured on 40 different crystallites, spread out on 7 independent images at the same magnification. Each *d*-spacing is determined on a coherent domain corresponding to the stacking of about 15 planes on average. Measurements result in the high mean value of 0.347 ± 0.008 nm compared with 0.330 nm for a highly ordered hexagonal BN structure. This deviation expresses a turbostratic feature from the ceramic signifying there is a two-dimensional ordering with atomic plan disorientations. According to the classification of More et al.[2] this *d*(0 0 0 2) spacing in the range of [0.340–0.355 nm] corresponds to a *meso-graphitic* structure.

All the obtained values were also plotted as a function of the coherence domain length Lc (Fig. 10). Obviously, the *d*(0 0 0 2) spacing of larger crystallites tends toward a constant value close to 0.34 nm in opposition to the broader distribution of the smaller ones that seem to be more sensitive to the microstrain or plane distortion than the larger ones. Besides, the observed difference

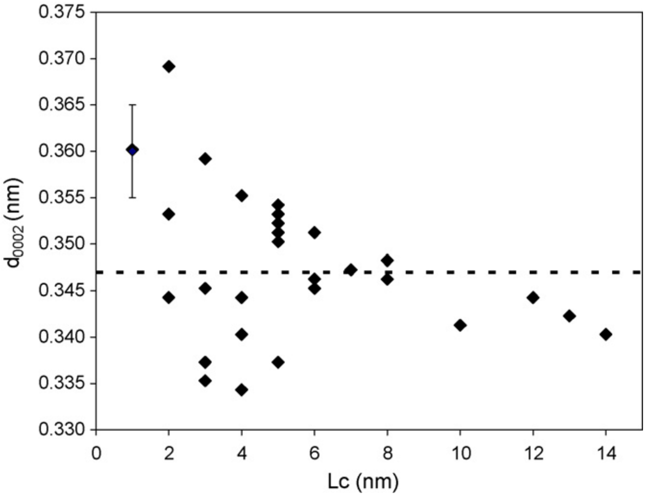

Fig. 10. BN-*d*(0 0 0 2) lattice spacing vs. the coherence length Lc. The dotted line corresponds to the means value (0.348 Å).

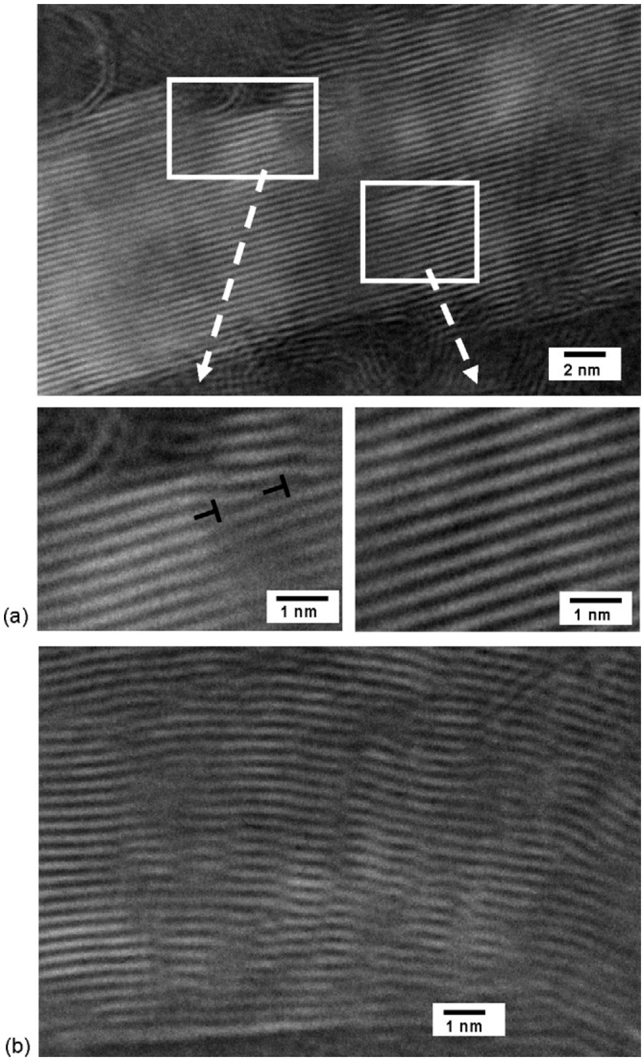

Fig. 11. (a) HR-TEM image of a large BN crystallite. Enlargements reveal a perfectly ordered area (right) and a faulted area (left), (b) HR-TEM image of a faulted BN crystallite.

from a graphitic BN structure would be partly explained by the presence of impurities (oxygen or carbon) in the unit cell. Perfectly crystallized hexagonal BN coexists with turbostratic BN. That is illustrated in Fig. 11. The first HR image (Fig. 11a) exhibits a large h-BN crystallite with a well-crystallized core as evidenced by the straight fringes while the edge reveals some defaults like dislocations and bent lattice fringes. The second image (Fig. 11b) shows a faulted t-BN (turbostractic BN) grain with wavy (0 0 0 2) lattice fringes and dislocations.

Of the same order, diffractograms obtained by numerical Fast-Fourier Transformations (FFT) from TEM HR images allow another type of sharp lattice fringes to be observed in addition to the basal fringes (see Fig. 12). According to the calibration, the inter-planar spacing measurement indicates 0.21 nm that corresponds to the $(1\,0\,\bar{1}\,0)$ or $(1\,0\,\bar{1}\,1)$planes of the h-BN structure ($d_{10\bar{1}0} = 0.216$ nm and $d_{10\bar{1}1} = 0.206$ nm for perfect h-BN). However, the angle of the corresponding lattice fringes with the (0 0 0 2) lattice fringes equal to 74° lead to confirm the (1 0 −1 1) plane (72° for the theoretical angle).

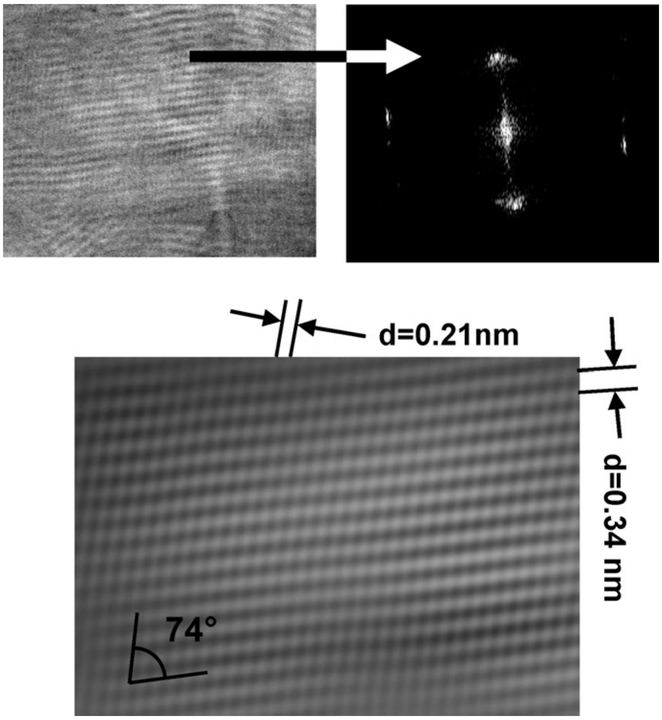

Fig. 12. Microdiffractograms (image) obtained by numerical fast Fourier transform (FFT) from HR-TEM image.

3.4. EELS analyses

The interest of the present EELS analyses lies in the confirmation of the chemical composition homogeneity of the BN deposit through a quantitative study. For that purpose, 20 spectra have been recorded at various layer locations. Analyses were performed in TEM imaging mode with an illuminated area of 100 nm.

As an example, the EELS spectra of BN coating obtained at the end of 80 min is given in Fig. 13. It shows the two distinct absorption peaks starting at 188 and 400 eV and corresponding to the known K-shell ionization edges for boron (B–K) and nitrogen (N–K), respectively. The fine structure examination confirms the sp2 hybridization state typical of the hexagonal

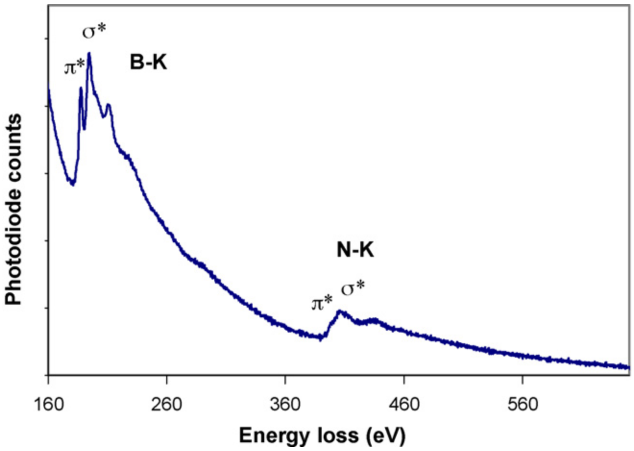

Fig. 13. EELS spectrum from a hex-boron nitride sample obtained after 80 min deposition.

BN[10] (a first sharp peak corresponding to the 1s → π* transition, followed by a broader peak due to the 1s → σ* transition).

All the analysed spectra suggest the same scheme with a few exceptions. None of them detect oxygen contrary to the occasional presence of the C–K edge in the analysed area. C/B ratio stays nevertheless lower than 0.1 while the N/B ratio remains very close to one, ranging from 0.83 to 1.05 with a mean value of 0.95 that is consistent with the previous AES analysis. Finally, the great similarities between all the spectra seem to show a homogenous BN both along the fibre and through the thickness of the deposit.

4. Conclusion

The use of the TDMAB/NH_3/H_2 gaseous system for the synthesis of hexagonal boron nitride by CVD process has been demonstrated and discussed in this present study. BN was deposited on carbon fibres with a controlled thickness in the range 0.1–5 μm at 1300 °C. Due to the high resistivity of the carbon, the heating was successfully performed by Joule effect through the substrate.

From a chemical point of view, the combined results from AES with EELS support the stoichiometry 1:1 between boron and nitrogen. The BN/fibre interfaces analyses show a penetration of the carbon element within the deposit which probably occurred at the start of the layer growth. The deposits appear to be free of significant amounts of impurities.

As for the general microstructure, TEM analysis describes the crystal as meso-graphitic hexagonal BN for which perfectly organized BN coexists with a turbostratic form. Numerous elongated and varied size crystallites were perceived within the layer with (0 0 0 2) lattice fringes parallel to the long axis.

In conformity with previous works,[11] the degree of order could be certainly improved with a high temperature treatment (beyond 2000 °C).

Acknowledgements

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