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Transmission electron microscopic investigations on SiC- and BN-coated carbon fibres

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Carbon fibres were coated with layers of silicon carbide (SiC) and boron nitride (BN) by conventional chemical vapour deposition. The SiC films were deposited by thermal decomposition of methyltrichlorosilane, whereas the BN films were deposited using the stepwise disproportion reaction of boron chloride with ammonia. Samples for electron microscopic investigations were prepared by separating film from fibre or by conventional mechanical thinning and subsequent ion milling of cross sections of coated fibres. Bright- and dark-field images of both planar and cross-sectional electron microscopic investigations on the fibre coatings gave detailed information on film thickness and morphology. High-resolution images improved the structural information of electron diffraction patterns. Crystal dimensions in the SiC film vary between 10 and 40 nm. Electron diffraction revealed the crystal structure to be a mixture of disordered hexagonal 2H-SiC and cubic β-SiC. High-resolution images showed the (1 1 1)-planes to be preferred for deposition. In BN films, a hexagonal turbostratic structure similar to turbostratic carbon was observed. Apart from amorphous regions, nanocrystalline parts were detected, which have a higher structural perfection in the stacking sequence of their (0 0 2)-planes compared to the (0 0 2)-planes of the turbostratic carbon fibre. High-resolution images located the film–fibre interface that was confirmed by electron energy loss spectroscopy.

1. Introduction

An important subject in current material research is the design of advanced composite materials for applications, e.g. in vehicle and aircraft construction, under conditions of extreme mechanical stress. Fibre-strengthened composites will become increasingly significant due to their favourable mass-to-strength ratio. The reinforcement and/or binding effects of the fibres are widely influenced by coatings acting as diffusion barriers, sliding layers, adhesive agents or oxidation preventing films.

Starting from initial laboratory-based research [1], semi-technical systems for the multi-stage coating of endless fibres by means of chemical vapour deposition have been established. The deposited layers have been characterized in detail by a range of solid-state analytical methods like SEM, X-ray spectroscopy for microanalysis (ESMA), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and Raman scattering [2–4]. However, all these methods failed to give detailed information on the film thickness and uniformity, crystal dimensions in the range of nanometres and the quality of the layer–fibre interface. Transmission electron microscopic investigations on cross-sections may overcome this problem. Moreover, the film structure and their orientation relationship to the carbon fibre may be observed by high-resolution imaging.

2. Experimental procedures

Prior to the deposition, the sizing of the endless carbon fibre bundle or roving (PAN-fibres T800 HB-40B, 6k) was removed thermally. Silicon carbide films were deposited continuously by thermally enhanced chemical vapour deposition in a modified commercial system from the semiconductor technology. Three steps are possible in the multi-stage coating system: desizing, pyrolytic carbon coating and silicon carbide coating. A schematic representation of the equipment consisting of the furnace unit, the drive assembly for fibre roving transport, the gas supply and waste elimination, as well as the most important process parameters, is given elsewhere [2]. The central pyrolysis reaction is the decomposition of methyltrichlorosilane at 1273 K, which occurs in hydrogen or argon as carrier gases at normal pressure to enable a continuous coating of the endless fibres.

A similar system has been constructed for the deposition of boron nitride films on desized carbon fibres [4]. The stepwise disproportion reaction of boron chloride with ammonia takes place typically at a temperature of 1123 K. The reactants were diluted in argon at normal pressure to establish the continuous BN deposition on the endless carbon fibre roving similar to the SiC process. Good infiltration into the multifilament bundle is reached by the proper choice

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of gas flow conditions and the velocity of roving transport through the reactor.

Samples for transmission electron microscopic investigations were prepared in two ways. In the case of the planar inspection of the films, the carbon fibres were removed by thermal treatment in air at 773 K. The SiC and BN coatings exhibit a good oxidation resistance at this temperature and form hollow tubes. Because their thickness is below 100 nm, the remaining film is electron transparent. In the case of fibre cross-sections, multifilament bundles were glued between silicon wafers with epoxy Gatan G1. These silicon–fibre–silicon sandwiches were prepared to a thickness of several micrometres by conventional mechanical grinding and polishing on diamond lapping films up to 0.1 μm grain size. By subsequent milling with argon ions of energies between 5 and 3 keV, the samples were thinned to electron transparency.

For transmission electron imaging and diffraction, as well as energy-dispersive X-ray spectroscopy (EDX) measurements, a 200 kV Hitachi H-8100 was used. Parallel recorded electron energy loss spectroscopy (PEELS) was performed in a 200 kV Phillips CM 20 fitted with a Gatan 666 spectrometer.

3. Results

3.1. Morphology and structure of SiC films

Figs 1 and 2 show electron micrographs of a typical silicon carbide layer in the bright- and dark-field image. The (2 2 0) and the (3 1 1) Bragg reflections were used to obtain the dark-field image, where individual grains are clearly visible. The size of these microcrystallites lies between 10 and 40 nm. The film which was separated from the fibre provides additional information about the fibre morphology by means of the surface replica technique. The well-known fibrillar surface of PAN-fibres with extrusion marks parallel to the fibre axis [5, 6] caused the darker stripes of about 50 nm width in the bright-field image. Figs 3 and 4 show a cross-section of the SiC layer on a carbon fibre in bright- and dark-field electron microscopic images. They reveal a uniform thickness of the film of about 40 nm with a satisfactory film adhesion to the fibre. The grooves caused by extrusion are completely covered and partially filled. The average SiC grain size is equal to the grain size in the images of planar investigation (Figs 1 and 2) and does not seem to be changed by the various techniques of electron-transparent specimen preparation.

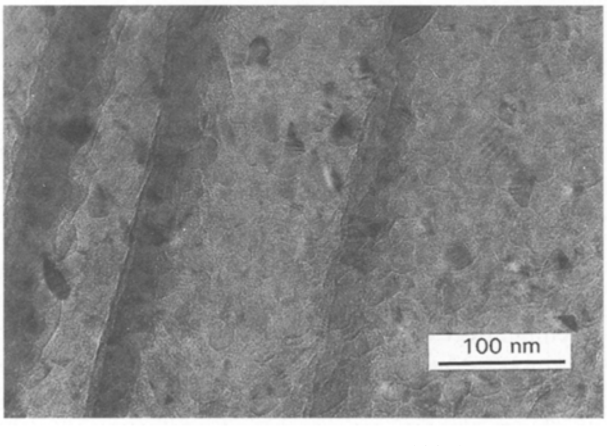

Figure 1 Bright-field image of the silicon carbide layer.

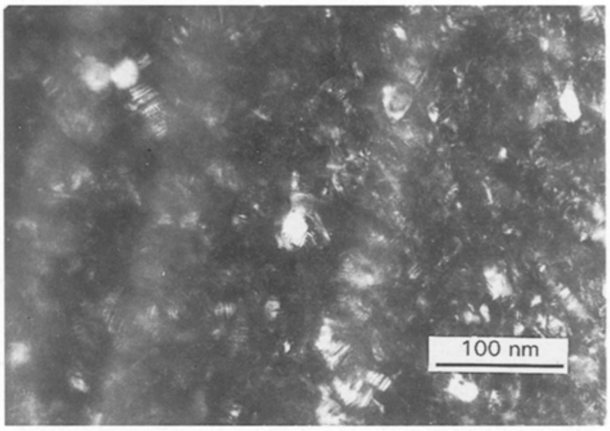

Figure 2 Dark-field image of the silicon carbide layer.

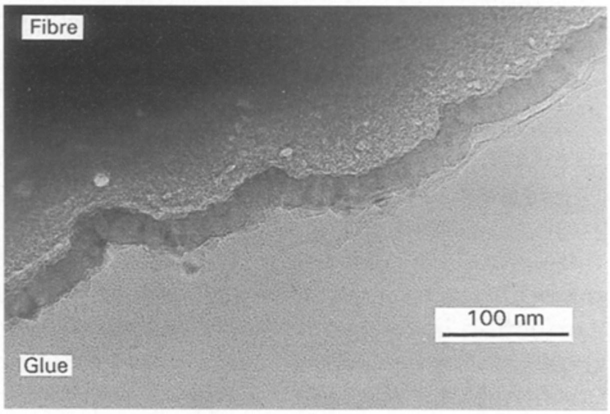

Figure 3 Bright-field image of a SiC-coated fibre (cross-section).

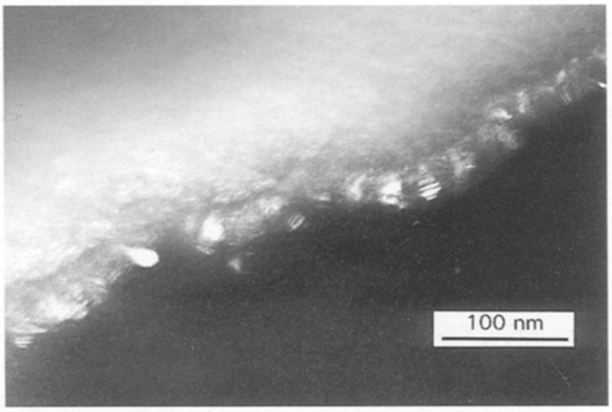

Figure 4 Dark-field image of a SiC-coated fibre (cross-section).

Fig. 5 demonstrates the *n*-beam lattice image of the transverse cross-section of film and fibre, which reveals the flat (1 1 1)-planes of cubic β-SiC with 0.252 nm spacing and the curvilinear (0 0 2) hexagonal ring planes of turbostratic carbon with 0.34 nm

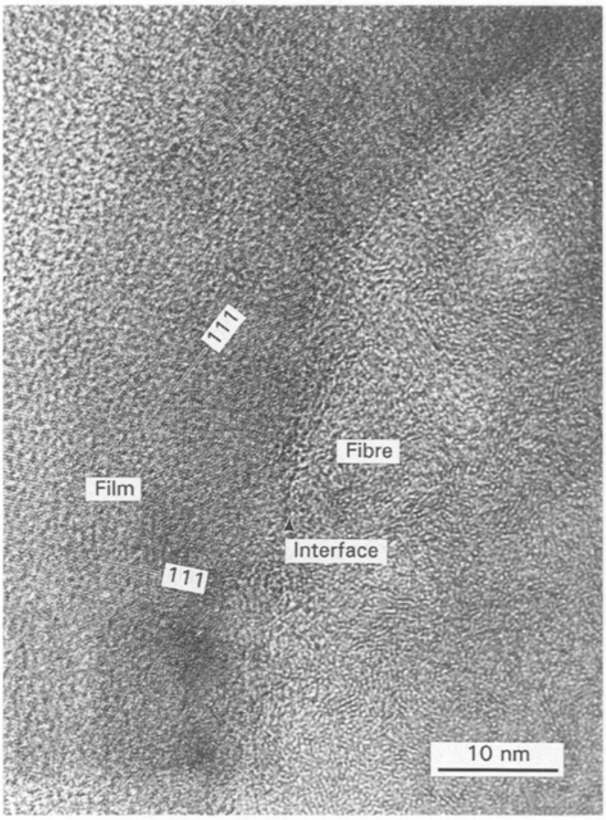

Figure 5 N-beam lattice image of a SiC-coated fibre (cross-section).

spacing in the fibre. These planes are folded extensively. The crumpled sheets are aligned to the carbon fibre axis and form voids or areas of low density located at the fibre surface under a skin region of a few nanometres. Such porous areas are clearly visible as lighter parts in Fig. 3 and correspond to the fibre model presented by Johnson [5] and others. At the interface between the SiC layer and the carbon fibre, a pyrolytic carbon film with a thickness of less than 5 nm is suggested by the higher degree of order of the (0 0 2) carbon atom-layer planes closely aligned to the fibre surface. Owing to the very similar structure of the fibre skin region it is not possible to distinguish between the fibre and such a thin pyrolytic carbon film by means of high resolution TEM (HRTEM). The deposition of these extremely thin films has been revealed by Raman spectroscopy [7].

3.2. Electron diffraction results on SiC films

Fig. 6 shows the diffraction pattern of transmitted electrons (TED) on the SiC coating perpendicular to the former fibre surface. The diffraction rings may be indexed by the planes of cubic β-SiC with exception of the (2 0 0) and (4 0 0) Bragg reflections. The disappearance of these two diffraction rings and the presence of an additional hexagonal (1 0 0) ring (wurtzite structure) in the TED pattern distinguishes it from well-crystallized cubic β-SiC. These features may be understandable with respect to the well-known polytypes of layer compounds. Spallerite with an ABCABC layer sequence and wurtzite with an ABAB layer sequence are known as well-ordered basic structures. Chin *et al.* [8] calculated the X-ray diffraction pattern for a completely random layer sequence, 1H, that agrees satisfactorily with our electron diffraction pattern. Therefore, we consider the fibre coating to be a mixture of disordered hexagonal 2H-SiC and cubic β-SiC.

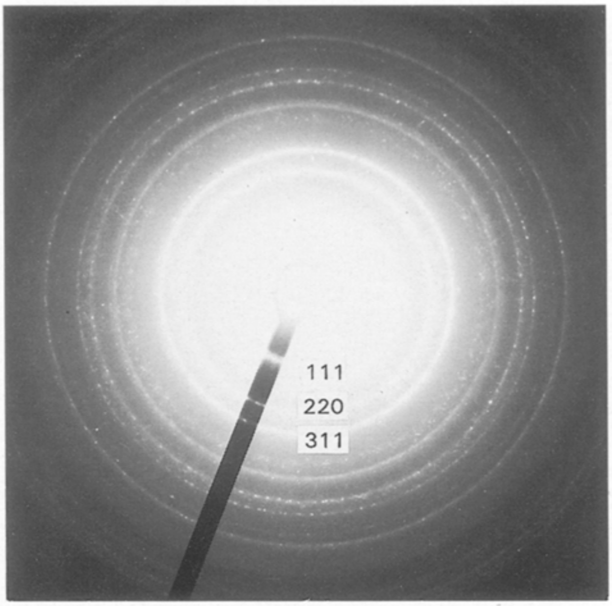

Figure 6 Electron diffraction pattern of the SiC layer.

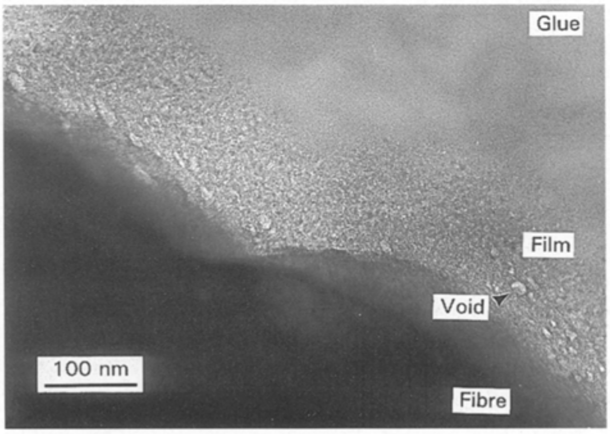

Figure 7 Bright-field image of the transverse BN film/fibre cross-section.

3.3. Morphology and structure of BN films

Figs 7 and 8 show the cross-sections of boron nitride-coated fibres observed in the transverse and longitudinal direction. Both bright-field images show the above described morphology of the carbon fibre with extrusion marks and needle-shaped voids with diameters of about 10 nm perpendicular to the axis (Fig. 7) and a length of about 100 nm parallel to the axis of the fibre (Fig. 8). Only the outside part of the fibre with the BN coating has been thinned sufficiently for transmission electron microscopic investigation. The boron nitride film with an average thickness of 100 nm adheres especially well to the fibre surface. TED patterns show the hexagonal structure of BN with partially preferred orientation of microcrystallites as well as amorphous parts. High-resolution images of the films

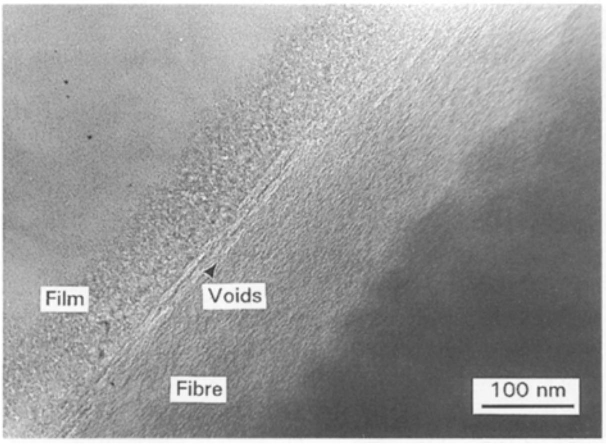

Figure 8 Bright-field image of the longitudinal BN film/fibre cross-section.

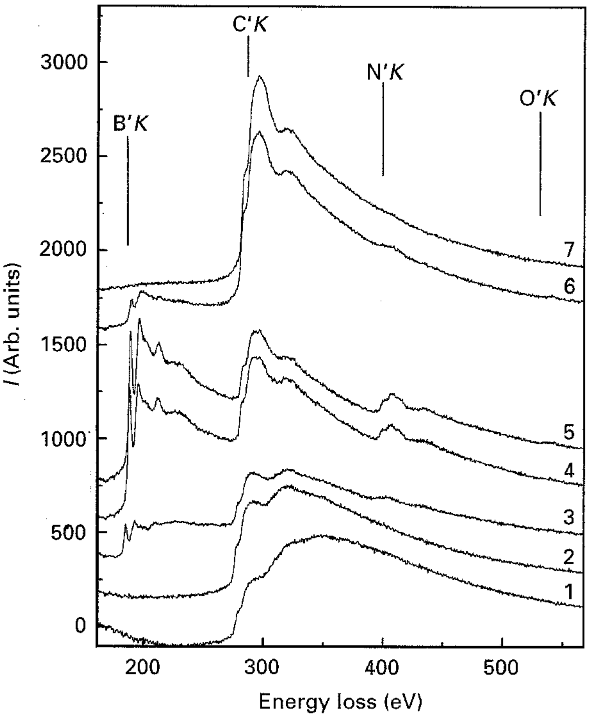

Figure 9 Electron energy loss spectra across the BN film/fibre cross-section. 1 and 2, carbon fibre; 3, film–fibre interface; 4 and 5, BN film; 6, film surface; 7, epoxy glue.

(Figs 10–12) reveal a turbostratic structure very similar to that of the fibre with a spacing of $d_{002} = 0.367$ nm. This is easy to understand, because hexagonal BN has nearly the same atomic distances as graphite with only alternating boron and nitrogen atoms at the carbon sites [9, 10]. Electron micrographs with magnifications of about 300 000, which allow a survey of the whole coating, are insufficient to locate the transition from the film to the fibre.

Therefore the position of the interface between turbostratic carbon and turbostratic boron nitride had to be determined by detection of the elemental composition. With a 2 nm diameter electron beam, the interface region has been probed by means of electron energy loss spectroscopy with parallel energy recording (PEELS). We measured the spectra of seven irradiated points on a line across the BN-coated outer part of the fibre that was embedded in epoxy glue for preparing the cross-section. The spectra (Fig. 9) reveal the *K*-edges of film components like boron, carbon, nitrogen and oxygen with electron energy losses between 100 and 600 eV. The origin of the oxygen content in the range of 10 at % is not clearly identified.

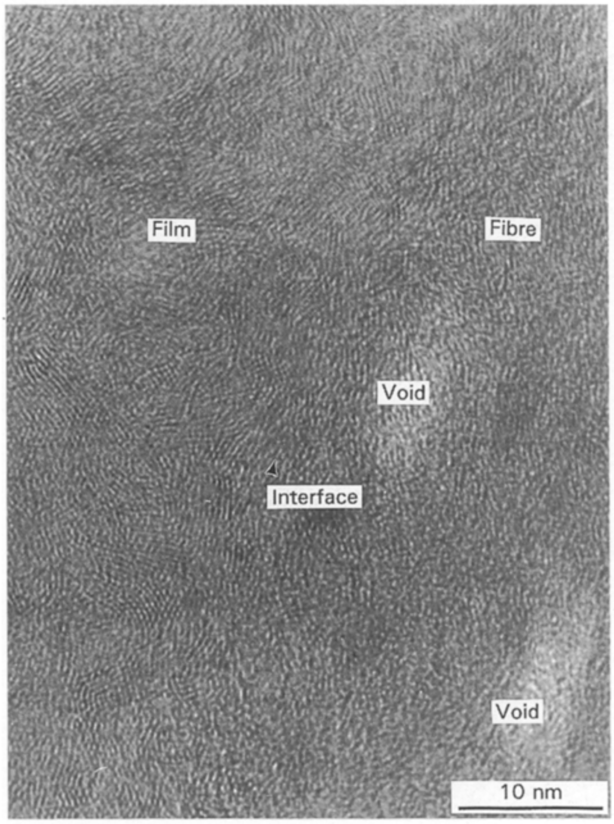

Figure 10 High-resolution image of the BN-coated fibre (transverse cross-section).

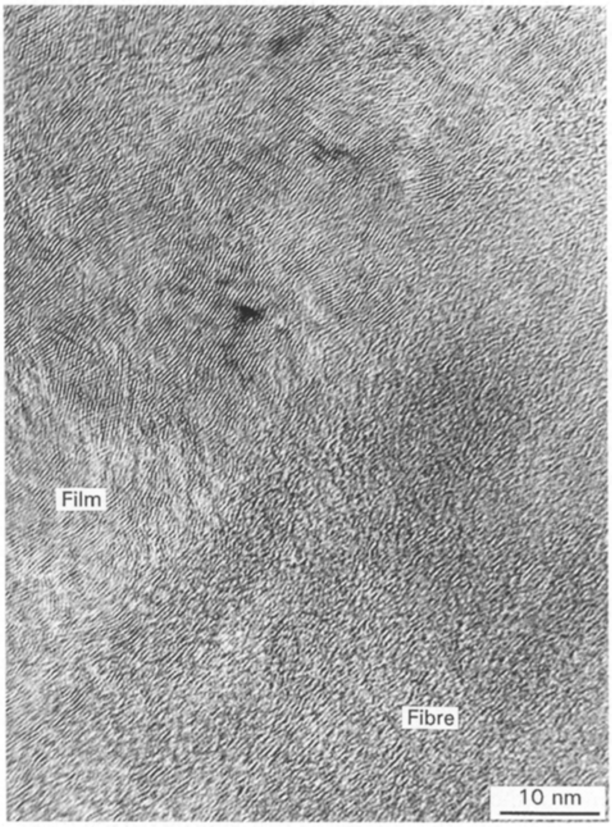

Figure 11 High-resolution image of the BN-coated fibre (longitudinal cross-section).

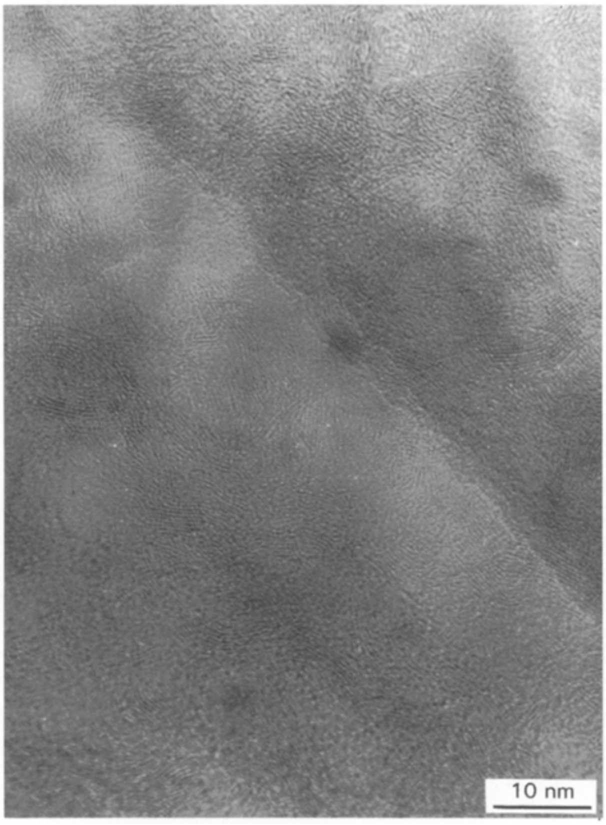

Figure 12 High-resolution image of the BN layer (planar view).

Cholet *et al.* [11] proposed the existence of highly hygroscopic intermediate solids like boron amides and imides in chemical vapour deposited BN films. The third PEELS spectrum in Fig. 9 has been related to the transition from film to fibre.

Figs 10 and 11 show high-resolution images of transverse and longitudinal cross-sections of the BN-coated fibre. In both micrographs, the striking feature is the higher structural perfection in the orientation of the (0 0 2) BN hexagonal ring planes to each other, as well as the evidence of the higher structural perfection in the stacking sequence of these planes compared to the (0 0 2) C aromatic ring planes. This perfection is limited to small volumes in the range of several cubic nanometres. The high-resolution image of the BN layer in planar view (Fig. 12) confirms that the (0 0 2) planes are randomly folded in all room directions and form nanocrystals. A detailed inspection of the film–fibre interface provides a relationship of the structure and growth characteristics of the film. The frequent changes of growth direction of the (0 0 2) atomic layers in the boron nitride film seem to be mainly caused by the growth of adjacent hexagonal ring layers. Such sterically limited or influenced growth of curvilinear (0 0 2) planes which bend off the original direction parallel to the surface may be observed also in the case of pyrolytic carbon films. Under convenient deposition conditions, the growth of the (0 0 2) planes firstly takes place parallel to the carbon fibre surface. The real fibre surface-morphology with extrusion marks causes the curvilinear (0 0 2) hexagonal ring layers to deviate from their original direction and to show the same curls in boron nitride films as well as in carbon films [12]. Dugne *et al.* [10] suggested a more kinetically-based boron nitride deposition model on the basis of their transmission electron microscopic analysis of coated fibres. The lattice images exhibit the same features described above, except that the micropores in the BN film were not observed.

A convenient high surface temperature of the film after deposition enables the outer (0 0 2) hexagonal ring planes of the film to relax and become arranged parallel to the film surface. This makes them preferable to act as inner sliding faces. By temperature quenching after BN film deposition, the unoriented (0 0 2) hexagonal ring planes, may not relax. Possibly they decrease the sliding efficiency of the deposition. On the other hand, in boron nitride films as well as in pyrolytic carbon films on very smooth fibres made of glass or silicon carbide (Nicalon), these hexagonal ring planes remain aligned to the fibre surface over a film thickness of more than 20 nm [12].

4. Conclusion

Chemical vapour-deposited SiC coatings on carbon fibres have been prepared by pyrolysis of methyltrichlorosilane. Electron-transparent cross-sections of SiC-coated carbon fibres revealed a nearly uniform layer thickness of about 40 nm with filled extrusion marks at the fibre surface and reasonable adherence to the fibre. The layer consists of microcrystallites up to 40 nm. The crystal structure has been described as a mixture of cubic β-SiC and disordered hexagonal 2H-SiC, which is common for CVD SiC deposits and well known as one polytype of layer compounds with a random layer sequence.

BN coatings on carbon fibres were deposited by the stepwise disproportion reaction of boron chloride with ammonia. Electron microscopic images of cross-sections show a uniform layer thickness of about 100 nm with coated extrusion marks and good film adherence. Both the carbon fibre and the BN film structure are hexagonal turbostratic. Therefore, the interface between film and fibre has been detected and confirmed by PEELS.

The hexagonal ring layer planes have been resolved by high-resolution electron microscopy. The curvature of the BN hexagonal ring planes is a striking feature and seems to be caused by their sterically hindered growth. Owing to the higher perfection in their stacking sequence compared to the aromatic carbon planes of the fibre, the BN films may be characterized as nanocrystalline.

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