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On the nature of boron–carbon–nitrogen compounds synthesised from organic precursors

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Abstract

Three compounds were prepared through pyrolysis of organic precursors, namely pyridine-borane, piperazine-borane, poly(acrylonitrile)-BCl_3, following the routes proposed in the literature for the synthesis of single-phase boron carbonitrides of various compositions. X-ray diffraction and MAS NMR studies performed on the powders obtained suggest that the resulting compounds are mixtures of amorphous boron and turbostratically distorted hexagonal boron nitride and graphite rather than substitutional solid solutions of all three elements in a honeycomb network, as was claimed previously. Such a conclusion is also consistent with the results of the XRD investigation of the samples after subsequent heat treatment at 1800–2000°C in argon and in nitrogen of atmospheric pressure.

Keywords: Nuclear magnetic resonance; X-ray diffraction; B–C–N compounds

1. Introduction

B–C–N materials have become the topic of a large number of research papers since the early seventies when the first reports [1,2] on synthesis and investigation of these ternary compounds appeared. Extensive, although not exhaustive, lists of publications on this subject can be found in Refs. [3] and [4].

Despite the numerous reports on obtaining boron carbonitrides in a variety of chemical processes using different precursors, there is still a lack of evidence that all or, at least, some of the reported B–C–N materials are substitutional solid solutions of all three elements in a honeycomb network rather than mechanical mixtures of graphite and hexagonal boron nitride both turbostratically distorted. Speculations on this particular matter along with a selection of approaches suitable for deciding or, more precisely, guessing the nature of the compounds obtained are found in Refs. [3–6]. Nevertheless, up to now there has been no convenient and versatile procedure to distinguish between the two sequences of the atomic arrangement mentioned above. Thus it is likely that with this object in view an accumulation of additional data from various experimental techniques as well as elaboration of new approaches to the data treatment are needed.

The present study was undertaken in an attempt to get further insight into the atomic arrangement of several "compounds" obtained through the pyrolysis of organic precursors and claimed to be boron carbonitrides.

2. Experimental details

2.1. Preparation

All organic precursors were purchased from Aldrich and used without further purification. Sample no. 1 was prepared following the route proposed in Ref. [6]: 10 g of pyridine-borane liquid placed under

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Ar (AGA, Sundbyberg, Sweden; claimed purity, 99.999%) atmosphere in a spherical flask with a volume of 1 l were heated in an oil bath up to 120°C at the average rate of 1°C $\min^{-1}$ with a subsequent isothermal hold for 3 h. The resultant orange solid was crushed under Ar and placed into an alumina vessel, which in its turn was inserted into a quartz tube of a tubular furnace. The pyrolysis was performed under flowing Ar with 5°C $\min^{-1}$ increase of temperature up to 1050°C with a subsequent isothermal hold for 80 min.

Piperazine-borane powder was used as a starting material for sample no. 2 [6]. The powder was placed under an Ar atmosphere into an alumina crucible, which was than isothermally held for 80 min at 1050°C in a tubular furnace in a flow of Ar.

Sample no. 3 was obtained by the reaction of poly(acrylonitrile) powder with BCl_3 gas [7]. The powder in an alumina crucible was placed into a tubular furnace and held under a flow of boron trichloride (Air Products, Keumiee, Belgium; claimed purity, 99.99%) at 400°C for 90 min. Afterwards the resultant powder was heated in flowing Ar at 1000°C for 8 h.

All three finally obtained samples (denoted as "as-synthesized") were black-coloured powders.

Further heat treatment of the samples at higher temperatures was performed for 24 h in a graphite element resistance furnace (Thermal Technology Inc. 1000-3560-FP-20) with a permanent Ar or N_2 (AGA; claimed purity, 99.999%) flow providing near atmospheric pressure.

2.2. Characterization

X-ray diffraction studies were performed with a Siemens D5000 diffractometer operating in a θ–θ mode of the Bragg–Brentano focusing scheme with $CuK\alpha_{1,2}$ radiation. Patterns were collected with a step size of 0.04° in 2θ and the typical counting time about 45 s per step.

Magic-angle spinning NMR ^{13}C and ^{11}B spectra were obtained at 75.43 and 96.23 MHz respectively using a Varian Unity Plus 300 spectrometer with a Doty Scientific probe accepting 5 mm o.d. rotors made of zirconia. For ^{13}C resonance the spectrometer operating conditions were: pulse angle 90°; recycle delay 30 s; number of transients between 1850 and 1950; spin rate between 8 and 9 kHz. In the case of ^{11}B, the conditions were: pulse angle 18°; recycle delay 1 s; number of transients 500; spin rate between 8.4 and 10.7 kHz. Chemical shifts are referenced to the signals for tetramethylsilane (^{13}C) (indirectly) and $Et_2O.BF_3$ (^{11}B). Spectra were obtained at ambient probe temperature but this was not monitored, and at the spinning speeds used increases of 10–20° above room temperature are likely.

3. Results

3.1. As-synthesized specimens

3.1.1. Powder diffraction studies

Fig. 1 shows diffraction patterns collected from the as-synthesized specimens. The patterns from samples nos. 1 and 3 are similar to those provided by the authors of Refs. [6] and [7] for $2\theta > 20°$. As is also the case with sample no. 2, they indicate the presence of turbostratically distorted graphitic phases with low crystallite dimensions along both *a* and *c* axes. However, the behaviour of the diffraction curve from sample no. 3 in the lower angle region is markedly different from that of the original paper (Fig. 1 in Ref. [7]). In the absence of any details of the diffraction technique used by the authors of Ref. [7], one can only guess from the unusually steep decay of the intensity curve on the low angle side of the *002* reflection that either the method used hardly provided reliable data in this particular region or a background subtraction procedure was applied. Apart from a fall-

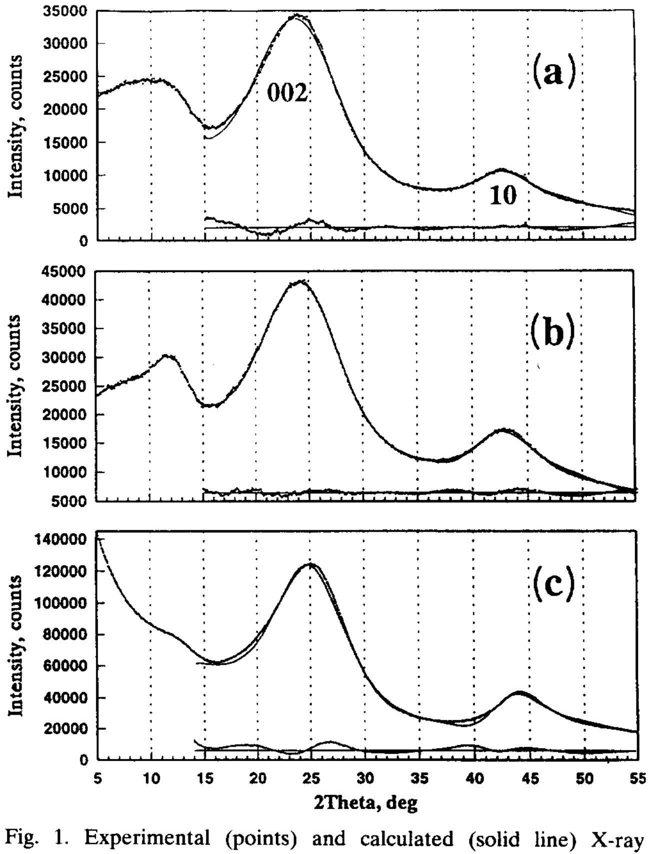

Fig. 1. Experimental (points) and calculated (solid line) X-ray diffraction profiles and difference curves of as-synthesised samples 1 (a), 2 (b) and 3 (c).

off in intensity from 0° towards larger θ values, typical for this type of structure, the pattern from sample no. 3 (see Fig. 1, trace (c)) contains an additional peak in the range from 10 to 15° which cannot be attributed to a graphite-like structure. The last feature is more pronounced in the patterns of the remaining two specimens (see Fig. 1, traces (a) and (b)). Even the mere fact that the substances obtained are not the single-phase ones raises doubts as to the compositions of boron carbonitrides obtained through elemental analyses and claimed [6,7] to be BC_4N, BC_2N and BC_3N for specimens synthesized in a very similar way to samples 1, 2 and 3, respectively. Realizing that the presence of a single peak is hardly sufficient for an unambiguous identification of a phase, we nevertheless assume that the peak at 10–15° can be attributed to amorphous boron. This is also supported by the fact that the peak remains after heat treatments while other peaks can vanish in response to structural changes [8].

Structural information on the graphitic phases present in the as-synthesized powders was obtained through a full-profile fitting of the diffraction patterns in the angular region containing *002* and *10* reflections. For this purpose the algorithm described in Ref. [9] was modified to include additional adjustable parameters, namely an integrated intensity and a full width at half maximum (FWHM) of a *002* reflection, an interplane distance, a mixing parameter for a pseudo-Voigt function representing the profile shape of a *002* peak and five additional coefficients for polynomial background approximation. As in the test case for the original algorithm [9], the peak shape of the *100* reflection from a commercially available boron nitride (Elektroschmelzwerk Kempten GmbH, Kempten, Germany; claimed purity 98%) was used as an instrumental function for the angular region of a *10* peak in the patterns of the samples under investigation.

For the reasons discussed below the fits obtained are very poor in the commonly accepted sense, since the goodness-of-fit indices are 4.0, 2.7 and 7.7 for traces (a), (b) and (c) of Fig. 1, respectively. Even so, the refined values of the parameters (Table 1) do provide a rough idea of the atomic arrangement because by and large the calculated curves follow the experimental profile shapes. A structurally ordered domain of the graphitic phases consists of two or three fairly parallel equidistant layers showing no registry as regards mutual arrangement and having relatively perfect in-plane ordering within circular regions ≈ 20Å in diameter.

Table 1
Refined values of in-plane lattice parameter (a) and crystallite size (L_a, equal to the diameter of a disk-shaped ordered region), interplane distance (d) and crystallite size (L_c, calculated from the Scherrer equation using the refined FWHM values) for the as-synthesized samples

Sample no.	a (Å)	d (Å)	L_a (Å)	L_c (Å)
1	2.600(2)	3.729(1)	22.6(6)	5.7(2)
2	2.4974(7)	3.6667(5)	20.14(2)	12.1(1)
3	2.44(4)	3.55(2)	21(2)	8.0(2)

The values of the in-plane lattice parameter hardly provide enough evidence that the ordered regions are in fact three-element honeycomb networks. Assuming that differences in the lattice parameters can be considered physically significant if they exceed 3σ, the a value of sample no. 1 coincides with that of a pure boron nitride ($a_{BN} = 2.50441(7)$ Å [10]). The a value of sample no. 2 is 2.4974 Å, which is less than a_{BN}, in agreement with the formation of a substitutional compound BC_xN claimed in Ref. [6]. At the same time a rough estimate of the composition is based on the model that the ternary compound is a substitutional solution of either carbon atoms in the BN network or equal amounts of B and N atoms in graphite. This leads to the x value:

$$x = (a_{BN} - a)/(a - a_G) \qquad (1)$$

($a_G = 2.465$ Å [10] is the in-plane lattice parameter of graphite and a that of sample no. 2) which is almost ten times less than that given in Ref. [6] (0.22 instead of 2). The big error margin of the a value of sample no. 3, in the strict sense, prevents unambiguous identification of the graphitic phase on the basis of the in-plane unit cell length. Nevertheless, even a visual inspection of the *10* peak in Fig. 1, trace (c), is enough to notice an essential shift of the peak position towards higher angles in comparison with the corresponding peaks in traces (a) and (b). The angular position of the peak corresponds to 44.1°, with the uncertainty, at most, ± 0.1°, while the analogous reflection from a circular ($D = 21$ Å) honeycomb layer consisting of carbon atoms only is found at 43.58° when calculated with the method of Wilson [11]. Hence, despite the low quality of the fit, it is safe to say that the a value for the graphitic phase in sample no. 3 appears to be substantially lower than that of graphite, which is highly improbable when the radii of the atomic species are considered [3].

Among the reasons which could cause both the lack of fit of the diffraction patterns and apparently lower a values the following seem to be the most plausible. (i) Neglect of additional unrevealed diffraction features from the amorphous boron phase in the angular region where the profile fittings were performed. (ii) Considerable variation of shape and/or ordering of the in-layer domain from being a disk with perfect honeycomb arrangement of constituent atoms. Extensive discussion on this matter can be found in Refs. [11]

and [12]. (iii) The graphitic phase under consideration is in fact a mixture at a nanometric scale of turbostratically distorted graphitic phases among which could be graphite, boron nitride and ternary phases composed of all three elements. In such a case an overlap of several (at least two) broad *10* reflections from such phases can manifest itself as a shape variation of the apparently "single" two-dimensional peak. The magnitude of this variation depends on crystallographic parameters and relative amounts of the constituent phases. As for the peak position, a mere reduction of the diameter of a graphite layer from 21 to 15 Å produces an offset of the maximum count of the *10* peak to the higher 2θ angle by 0.42°.

3.1.2. NMR investigation

Carbon-13 and boron-11 MAS NMR spectra for the as-synthesised materials are displayed in Figs. 2 and 3 respectively. In spite of the total spectrometer time for obtaining each ^{13}C spectrum (about 16 h), their quality is not high, since rather broad resonances in the region 100–200 p.p.m. are observed. The situation is complicated by a background signal from the probe at ca. 113 p.p.m. This has been subtracted by computer for the spectra shown in Fig. 2. The absorptions are in the region expected for graphite, but the width indicates a considerable dispersion of chemical environments and/or lack of crystallinity ("amorphous" sp^2-hybridized carbon). The variations between samples are significant but impossible to interpret with any certainty. Contrary to the suggestion in Ref. [6] (not supported by Fig. 5 of that paper) there is no indication of signals from B_4C, which should appear at $\delta_C = 1$ and 82 p.p.m. (the former being more intense). The ^{11}B spectra show maximum intensity at ca. -2 p.p.m. with a high-frequency shoulder. This shoulder seems to be least pronounced in sample 2. The spectra contain spinning sidebands, in which the major peak has a much reduced intensity. We interpret these spectra as a superposition of those expected for hexagonal or turbostratic boron nitride and amorphous boron. Authentic samples of the latter show a single band (Fig. 4) at 0 p.p.m., with relatively little intensity in sidebands, whereas the former gives a powder pattern typical of second-order quadrupolar interactions, with a doublet appearance, the maxima being at 20 and -4 ppm (Ref. [13] and Fig. 4). The spinning sidebands are quite prominent in this case and, in principle, spread over a very wide frequency range. Presumably the low-frequency maximum of the "doublet" overlaps with the amorphous boron peak to give the principal signal seen for the as-synthesized samples. We believe there

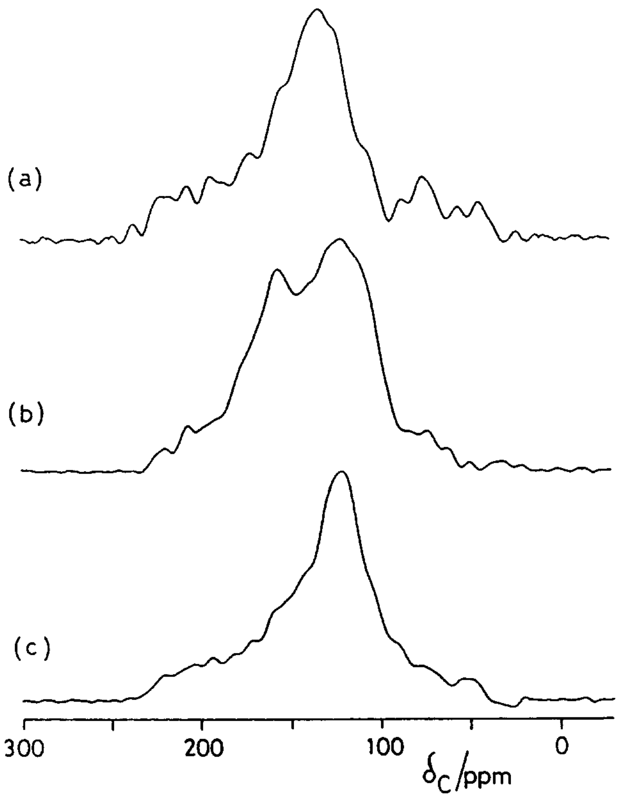

Fig. 2. 75.43 MHz ^{13}C MAS NMR spectra of (a) sample no. 1, (b) sample no. 2 and (c) sample no. 3. For the spectrometer operating conditions, see the text.

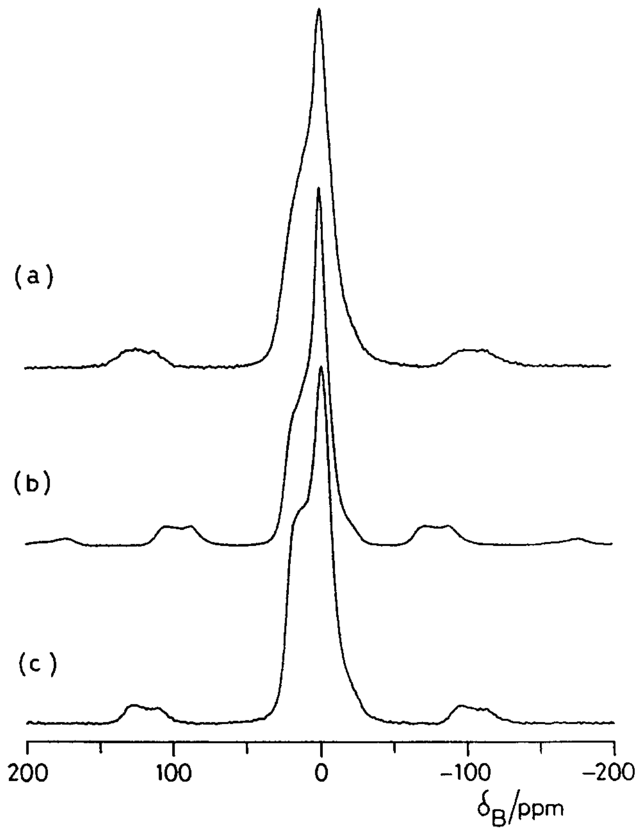

Fig. 3. 96.23 MHz ^{11}B MAS NMR spectra of (a) sample no. 1, (b) sample no. 2 and (c) sample no. 3. For the spectrometer operating conditions, see the text.

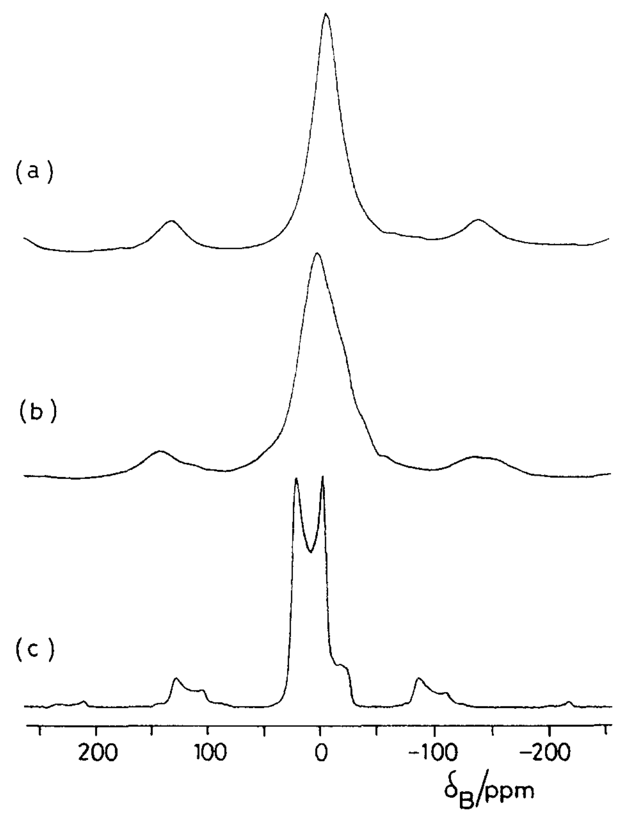

Fig. 4. 96.23 MHz ^{11}B MAS NMR spectra of (a) boron carbide, (b) amorphous boron, and (c) hexagonal boron nitride.

is some evidence for amorphous boron in Fig. 6 of Ref. [6], but unfortunately no spectrometer operating conditions are given in that paper, so comparisons with our NMR studies are problematic. Our conclusions are reinforced by subtracting the ^{11}B spectra of samples 1 to 3 from each other. This procedure makes it clear that the differences lie mostly in the relative amounts of a BN-type band and a broad band like that of amorphous boron. Although the latter might arguably arise alternatively from boron carbide (see Fig. 4), the absence of B_4C signals in the ^{13}C spectrum shows this is not the case.

3.2. Heat-treated specimens

According to Ref. [6] piperazine-borane- and pyridine-borane derived compounds irreversibly decompose at $T > 1800$°C in Ar atmosphere giving a mixture of BN, B_4C and C accompanied by a release of nitrogen. This conclusion, as well as the equation of the decomposition reaction at 2200°C also presented in Ref. [6], were deduced on the assumption that the starting compounds were single-phase boron carbonitrides of the compositions mentioned above. As is shown in Section 3.1, the last statement is open to question. In an attempt to take a new view of this problem in the light of the results so far obtained in the present study, we also performed heat treatment of the as-synthesized samples in nitrogen and argon atmospheres at elevated temperatures.

As the diffraction patterns (Figs. 5 and 6, traces (a)) suggest, heating in nitrogen at 1800°C resulted in a decrease of the amount of the phase previously identified as amorphous boron in samples 1 and 2. Essential narrowing of both *002* and *10* diffraction peaks for all three samples (see also Fig. 7, trace (a)) is accompanied by an emergence of reflections at 33.4 and 38.8° from an unidentified phase. These reflections are most conspicuous at 1800°C in the pattern of sample no. 1 and make themselves evident in the patterns of the other two samples heated in nitrogen at 2000°C (Figs. 6 and 7, traces (b)). In addition to the decrease of FWHM, the shape of the *002* peaks in Figs. 5 and 6, traces (a), implies the presence of more than one reflection in this angular region. The same goes for the shape of the *10* reflections in the patterns of all three samples heated in nitrogen at 1800°C. The profile fitting performed in this particular angular region on

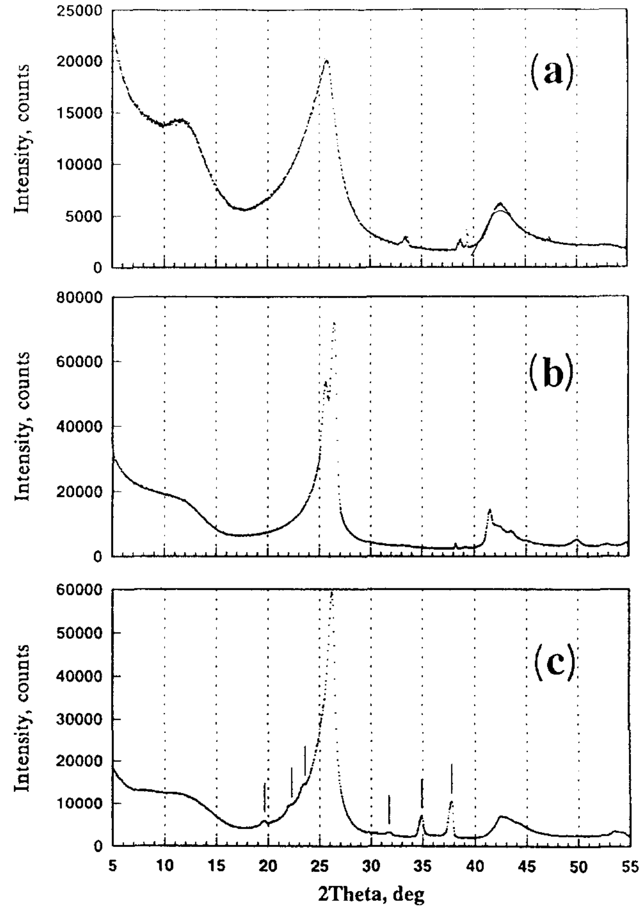

Fig. 5. Experimental (points) X-ray diffraction profiles of sample no. 1, heat-treated in N_2 at 1800°C (a) and 2000°C (b) and in Ar at 2000°C (c). The solid line shows the calculated profile of the *10* peak obtained in the course of profile fitting. Vertical bars indicate peaks belonging to the B_4C phase.

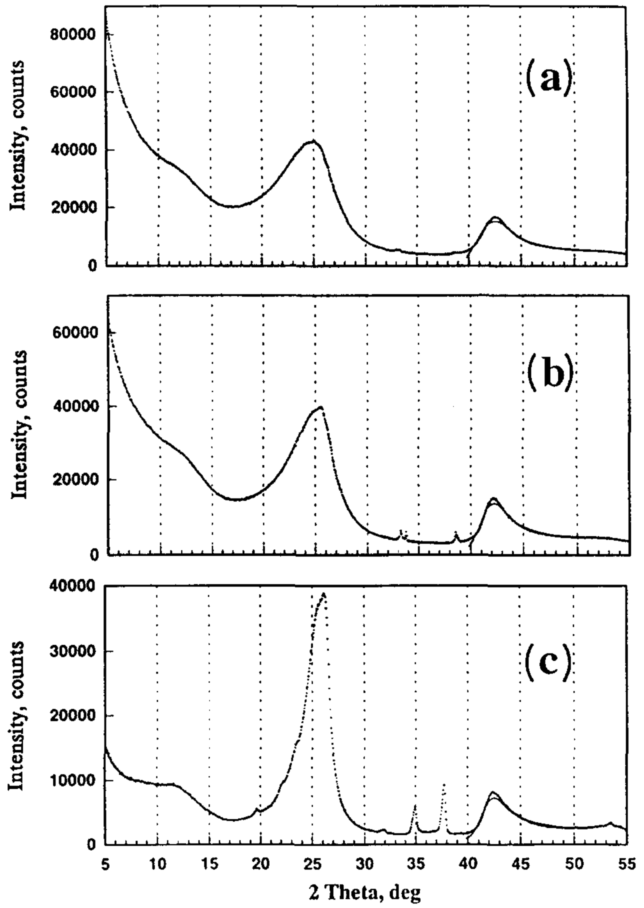

Fig. 6. Experimental (points) X-ray diffraction profiles of sample no. 2, heat-treated in N_2 at 1800°C (a) and 2000°C (b) and in Ar at 2000°C (c). The solid line shows the calculated profile of the *10* peak obtained in the course of profile fitting.

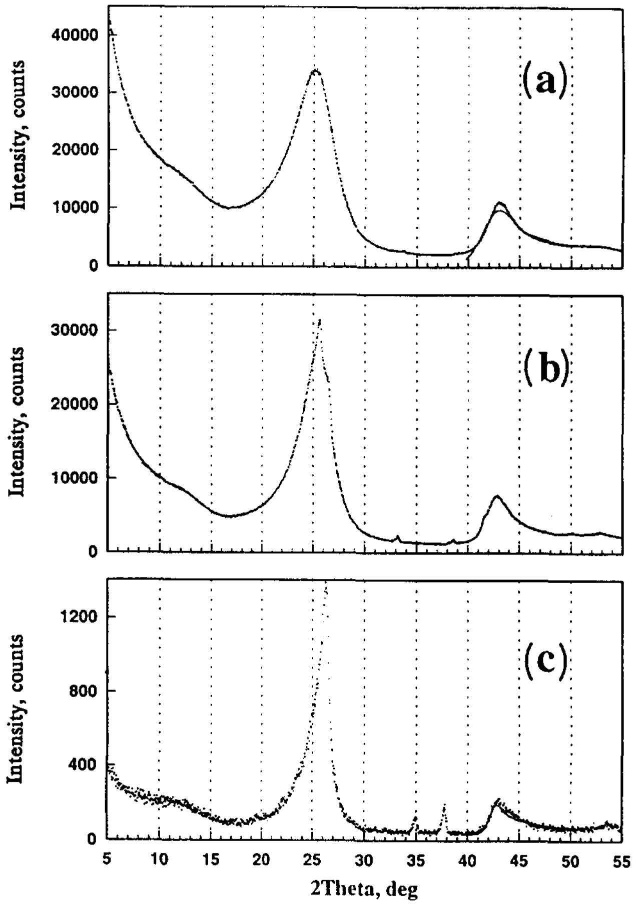

Fig. 7. Experimental (points) X-ray diffraction profiles of sample no. 3, heat-treated in N_2 at 1800°C (a) and 2000°C (b) and in Ar at 2000°C (c). The solid line shows the calculated profile of the *10* peak obtained in the course of profile fitting.

the assumption of a single peak present failed, displaying apparently systematic misfit.

The two-phase sequence becomes even more evident after heating in nitrogen at 2000°C, though in varying degrees for the different samples. Thus in this case the pattern of sample no. 1 (Fig. 5, trace (b)) contains two well separated *002* peaks belonging to different graphitic phases, one being three-dimensionally ordered since *101* (2θ|43.7°) and *102* (2θ|50.0°) reflections are present. Another graphitic phase according to the specific shape of the in-plane *10* peak exhibits only 2D ordering. Having the longer interplane distance (3.375 Å compared with 3.3281 Å [10] in a pure ordered BN), it is most likely that the layer stacking sequence of the 3D ordered phase is of the boron nitride type because the intensity ratio between *101* and *102* peaks resembles more closely that of BN (0.33) than that of C (5.02). As for the second phase, the sole value of the interplanar distance (3.465 Å) is not enough for its identification. It might be a turbostratically distorted graphite or any B–C–N phase. The phases found in the patterns of samples 2 and 3, heat-treated in N_2 at 2000°C (Figs. 6 and 7, traces (b)) seem to differ from those just mentioned by a smaller degree of ordering manifesting itself in bigger interplanar distances, broader peaks and absence of the 3D registry. Judging from the intensities of the corresponding *002* reflections the relative amount of phases is also different in each of the samples. When passing from sample no. 1 via no. 2 to no. 3, the amount of the BN-like phase decreases. Considering that a pure boron nitride is white, additional indirect evidence for the last statement can be found in the variation of colours of the resulting powders, which change from almost white with black inclusions (sample no. 1) through grey (sample no. 2) to almost black with white inclusions (sample no. 3).

In order to avoid a conceivable formation of the BN phase due to the reaction of amorphous boron with nitrogen, the heat treatment of the "as-synthesized" samples was also performed in an Ar atmosphere at 2000°C. Similar to the results reported in Ref. [6], such a treatment leads to the formation of a B_4C phase (Figs. 5–7, traces (c)). At the same time it is not obvious that this phase is a product of the decomposition of a ternary phase since simultaneously the relative amount of amorphous boron decreased. Thus it is not unreasonable to assume that when heated in an Ar atmosphere free boron present in the samples reacts with free carbon also available in the "as-synthesized" mixture, while on heating in ambient nitrogen it preferably forms a nitride. The behaviour of the low-angle shoulder of the interplanar peaks indicates the presence of more than one *002* peak in the patterns of the samples heat-treated in argon. An additional indication of a non-single-phase sequence arises from the misfit of the experimental curves made on the assumption of a single *10* peak present (see Figs. 6 and 7, traces (c)). For sample no. 1 the fitting procedure was not even carried out, since the deviation of the experimental diffraction curve (see Fig. 5, trace (c)) from the theoretical shape of a single in-plane reflection is visible to the unaided eye.

4. Discussion

On the grounds of the diffraction studies presented one can come to the conclusion that the methods of synthesis based on a solid phase pyrolysis of the organic precursors put forward in Refs. [6] and [7] do not provide single-phase ternary boron carbonitrides as was claimed by the authors. The resulting products are rather mixtures of amorphous boron and at least two turbostratically distorted graphitic phases with ordering on a nanometric scale, both within honeycomb layers and along the layer normal. Further heat treatment of the "as-synthesized" specimens leads to the increase of crystallite size (both intra- and interplanar), accompanied by the decrease of interplanar spacings and to the formation of either boron nitride or boron carbide (depending on the ambient gas) through the reaction of amorphous boron with nitrogen or carbon, thus anticipating that one of the graphitic phases in the initial mixture could have been a turbostratic graphite. Diffraction data hardly provide a means for a more precise identification of these, from the structural point of view, closely related phases because of the severe peak overlap. Although not mentioned yet, Raman spectra of the powders also obtained in the course of the present study do not contain any distinguishable peaks to clarify the phase sequence either.

NMR investigation sheds further light upon the nature of the as-synthesized materials. The NMR spectra are consistent with the suggestion that the samples are a mixture of amorphous boron and graphitic phases. The width of the ^{13}C signals suggests a substantial dispersion of chemical environments, though the boron spectra are consistent with the presence of boron nitride. The most likely interpretation is that the graphitic domains contain separate BN and graphite layers, perhaps in random intercalation. A single-phase ternary B–C–N system would be expected to give somewhat different spectra. The diffraction and NMR results give mutual support to these conclusions.

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