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Parametric study of the chemical vapour deposition of carbon–boron–nitrogen compounds

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The influence of various parameters controlling the chemical vapour deposition of carbon–boron–nitrogen mixtures has been studied using the experimental designs methodology which provides a valuable phenomenological approach for the initial study of complicated chemical systems. The gaseous precursors used were acetylene (C_2H_2), boron trichloride (BCl_3), and ammonia (NH_3). An extended experimental field was investigated, which leads to a very wide composition range for the deposits. All the deposits may be described as hexagonal single phase, including the C–BN–"BC_3" ternary domain. In this composition triangle, no thermodynamically stable boron carbides were found.

1. Introduction

Despite the results of Lowell [1], who has shown that the maximum substitution of boron for carbon in graphite is 2.35 at % at 2623 K, the very similar crystalline structure of graphite and boron nitride (Fig. 1) suggests the synthesis of alloys $C_x(BN)_{1-x}$ of these two materials.

The first attempt to achieve this was reported by Badzian *et al.* [2]; BCl_3, CCl_4, N_2 and H_2 mixtures, and chemical vapour deposition (CVD) was used at 2173 K to synthesize compounds which were characterized as substitutional solid solutions, although no composition was disclosed. Chen and Dufendorf [3] prepared C–BN coatings from mixtures of BCl_3, NH_3 and C_2H_2 at 1973 K, which, on the basis of electrical resistivity measurements and infrared spectroscopy were described as two-phase mixtures. More recently, Kouvetakis *et al.* [4] reported the synthesis of a graphite-like material of formula BC_3, by reacting C_6H_6 and BCl_3 at 1073 K. These authors also reported [5] the synthesis of materials whose composition was $C_{0.30}B_{0.35}N_{0.35}$ and $C_{0.03}B_{0.485}N_{0.485}$ from interaction of BCl_3, NH_3 and C_2H_2 at 673–973 K. They also obtained a hybrid [6] of composition C_2BN using CVD with BCl_3 and CH_3CN as starting materials at 11073 K. Moore *et al.* [7, 8] prepared samples of C–BN from mixtures of BCl_3, NH_3 and a hydrocarbon (CH_4, C_3H_8 or C_2H_2) at temperatures of 1773–2173 K. No precise composition was reported, but carbon contents of 3–65 wt % were indicated. It is noticeable that a B/N ratio greater than unity was registered for the high carbon rate deposits. These authors indicated that the "as-deposited" samples might be a single-phase mixture of carbon, boron and nitrogen. But compression-annealed samples examined were two-phase materials containing pure pyrolytic carbon domains and pyrolytic boron nitride ones instead of homogeneous substitutional compounds. Besmann *et al.* [9], on trying to obtain B_4C–BN mixtures, found a single-phase compound whose composition was $C_{0.43}BN_{0.29}$. A $C_{1.02}BN_{0.32}$ material was also synthesized, but it exhibited a second carbon phase.

It is noted that an electrically insulating compound has also been reported [10], obtained by hot pressing a mixture of BN and B_4C with additional sintering aids such as B_2O_3, magnesium or MgO. In addition, C–B–N materials were produced by Maya *et al.* [11–13] from the pyrolysis, in a closed vessel, of compounds such as aminoborane polymers [11] or borazine derivatives [12, 13]. Finally Montasser *et al.* [14] and Yamada *et al.* [15] used plasma chemical vapour deposition to synthesize B–C–N–H–(O) films.

Fig. 2 summarizes, in the C–B–N ternary diagram, the different compositions obtained by all these authors. It must be pointed out that although a very wide domain has been explored, no general picture emerges concerning the whole composition range of those C–B–N materials.

The conducting and intercalation properties of such compounds are expected to be intermediate between those of graphite, which is semimetallic, and those of boron nitride, which is an insulator. This behaviour offers incomparable opportunities for materials science research. This study was undertaken for these reasons and first of all to ascertain the conditions of C–B–N materials deposition and to determine the limits of composition which can be achieved by chemical vapour deposition. Secondly, the problem of the real nature of C–B–N materials was approached: are they simple mixtures of pyrolytic carbon and pyrolytic boron nitride at a nanometric scale or true substitution solid solutions of carbon for boron and nitrogen? This latter aspect will be further investigated.

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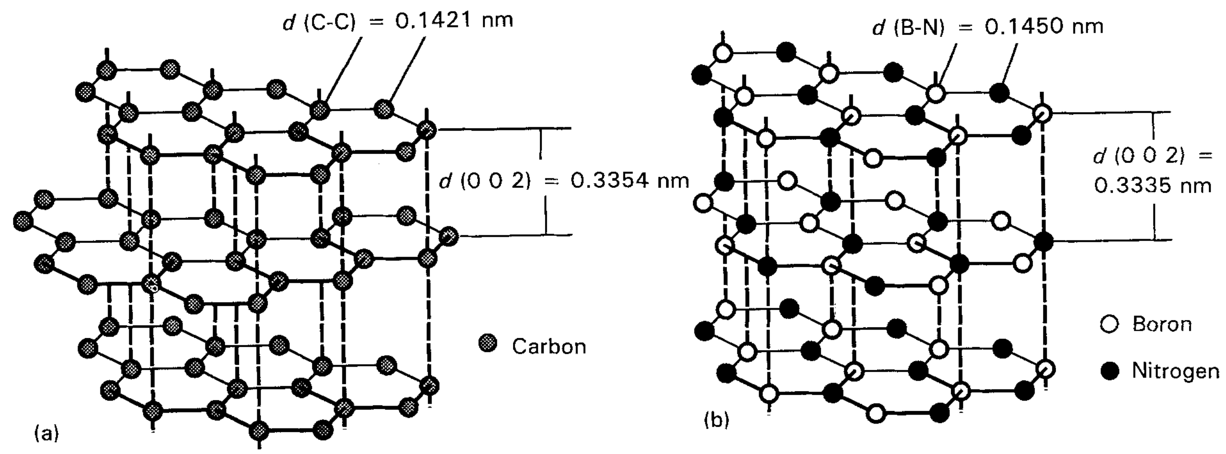

Figure 1 Crystalline structure of (a) graphite and (b) boron nitride.

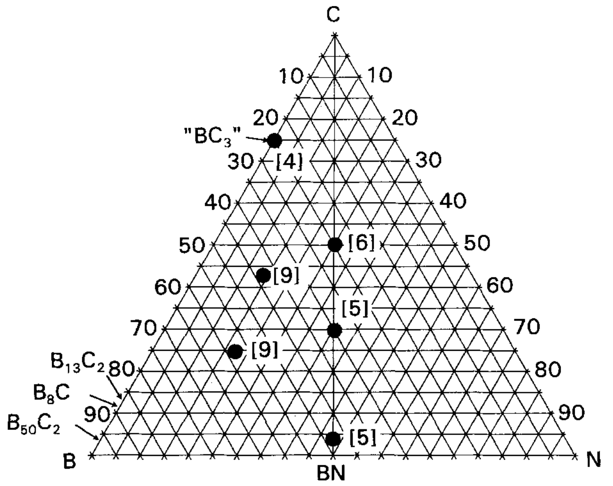

Figure 2 C–B–N composition diagram, showing the experimental values found by previous authors.

2. Experimental procedure

Coating was achieved in a classical alumina hot-wall reactor on silica glass samples (30 mm × 18 mm × 1 mm).

On the basis of the previous works mentioned above, the following gaseous precursors were selected: acetylene (C_2H_2), which is one of the hydrocarbons exhibiting a higher yield of decomposition; boron trichloride (BCl_3), which is the easier boron precursor to use; ammonia (NH_3) as the usual reducing agent for BCl_3; and hydrogen (H_2) as dilution and carrier gas. The initial total flow rate was kept constant and the gas flows were driven through mass flow regulators. Detailed data of the CVD apparatus are given by Saugnac *et al.* [16, 17] who initiated the present study.

3. Experimental design

Most of the experimental situations require the effect of varying two or more parameters to be examined. It has been shown [18, 19] that to obtain a complete exploration of such a situation, it is not sufficient to vary one factor at a time: all the combinations of the different factor levels must be examined in order to elucidate the effect of each factor and the possible ways in which one may be modified by the variations of the others. In this case, a generally useful technique is provided by the factorial experiment. When the expected number of experiments generated by the choice of the factors is too high, a fractional factorial design can be used. Many examples of such designs have been proposed in the literature.

In order to select an experimental design, we had to define the factors which were the independent variables, their variation range (lower and higher level for each factor) on the responses of the system; they were selected as follows.

Δm ($\mathrm{mg\,h^{-1}}$): the weight variation rate of the sample per unit time, calculated as the difference between the weight after and before deposition.

t ($\mathrm{\mu m\,h^{-1}}$): the coating thickness rate, measured by a spherical indentation using a rotating ball with an abrasive medium. Thickness is then calculated from the mean diameters of the ball prints measured through an optical microscope.

The composition of the deposit: in a ternary diagram, any composition is described by a set of two numbers. For reasons that will be clear below, the formulation $C_a(BN)_bB_{1-a-b}$ has been chosen. The translation to the most usual formula $C_xB_yN_{1-x-y}$ is simply done by the expressions: $x = a/(1+b)$ and $y = (1-a)/(1+b)$. These compositions were obtained by electron probe microanalysis (EPMA). Oxygen has always been found in negligible amounts, which permits the above composition formulation.

$d(0\,0\,2)$ (nm): the distance between two consecutive layers of the "graphitic" or, more appropriate, turbostratic structure of the C–B–N compounds which is always observed, as will be seen later. This distance is determined by X-ray diffraction analysis on the "as-deposited" samples (coating adherent to the substrate).

Many factors have a significant influence on the deposition process. The most important ones are temperature, T, total pressure, P, and initial gas phase composition. For a mixture $X(C_2H_2) + X(BCl_3) + X(NH_3) + X(H_2) = 1$, three composition parameters must be specified in order to fix the nature of the inlet gas stream. The variation ranges are determined from previous studies or experimental and technical limitations. Wide ranges are of interest, but the influence of a factor could be artificially magnified if the assigned variation is too important.

Temperature T: the lower level is fixed at 1123 K for kinetic reasons. In order to maximize the possibility of obtaining metastable materials (which might only have kinetic stability) with regard to thermodynamically stable products, the upper level is set at 1448 K.

Total pressure, P: between 10^3 and 6×10^3 Pa.

Molar fractions of acetylene, $X(C)$, and boron trichloride, $X(B)$: from previous experiments they range from 2×10^{-2} to 6×10^{-2} and 2×10^{-3} to 2×10^{-2}, respectively.

The molar fraction of ammonia was not chosen as the third composition parameter because of its very sensitive effect on homogeneous gas-phase nucleation [16].

Because the purpose of this study was to obtain C–B–N materials as dense coatings, it was more convenient to use the molar ratio NH_3/BCl_3 (N/B), varying from 10^{-1}–1. Therefore, the inlet gas phase was never poorer in boronated species than in nitrogenated ones.

The influence of these five factors and their combinations can be determined using a two-level complete factorial design. Experiments were then carried out for all the possible combinations of the two levels for these five factors, i.e. $2^5 = 32$. It is reasonable to assume that only first-order interactions are important and thus fewer experiments need to be carried out. At least two fractional factorial designs, 2^{7-4}, corresponding to 16 experiments are necessary to estimate independently the effects of the five main factors [20]. Table I summarizes the experimental conditions of these 16 runs and the corresponding responses. A minus (plus) symbol indicates that the parameter is set at its lower (upper) value.

4. Results of the experimental design

This factorial design gives the estimates of the effect (Table II) of the five main parameters and of seven aliases (linear combinations of interaction terms). The importance of each single interaction cannot be clearly specified without further experiments.

For each response of the system, the corresponding set of estimates allows the comparison of the relative

TABLE I Results of the experimental design

	T (°C)	P (mbar)	N/B	$X(B)$	$X(C)$	Δm ($mg\,h^{-1}$)	t ($\mu m\,h^{-1}$)	a (%)	b (%)	$d(002)$ (nm)
1	−	−	−	+	+	2.2	1.5	55.21	29.52	0.3833
2	+	−	−	−	−	0.3	0.5	78.97	2.77	0.390
3	−	+	−	−	+	0.1	0.5	70.89	8.00	0.394
4	+	+	−	+	−	10.8	5	80.28	0.00	0.346
5	−	−	+	+	−	15.3	13.8	6.55	63.45	0.363
6	+	−	+	−	+	2.3	8.8	80.69	9.45	0.341
7	−	+	+	−	−	1.3	1.3	56.8	31.06	0.3899
8	+	+	+	+	+	5.4	2.5	79.16	7.93	0.348
9	+	+	+	−	−	2.2	1.86	83.68	8.80	0.3403
10	−	+	+	+	+	8.1	3.8	30.61	65.84	0.3859
11	+	−	+	+	−	11.8	5.4	21.39	66.86	0.3735
12	−	−	+	−	+	0.8	0.4	69.26	30.58	0.3933
13	+	+	−	−	+	0.5	0.3	100.00	0.00	0.3451
14	−	+	−	+	−	8.3	3.5	80.07	5.50	0.3379
15	+	−	−	+	+	52.4	15	82.82	5.42	0.3423
16	−	−	−	−	−	0.1	0	49.12	1.11	0.3864

TABLE II Estimates of the influence of the factors and aliases for five responses

	Δm ($mg\,h^{-1}$)	t ($\mu m\,h^{-1}$)	a (%)	b (%)	$d(002)$ (nm)
T (°C)	3.09	0.91	11.78	−8.36	−0.013
P (mbar)	−3.03	−1.67	8.59	−5.13	−0.005
N/B	−1.72	0.72	−10.58	14.48	0.001
$X(B)$	6.67	2.30	−9.58	9.55	−0.006
$X(C)$	1.36	0.09	6.99	−1.43	0.000
$PX(B) + N/B\,X(C)$	−3.11	−0.95	4.43	−5.62	0.000
$TX(B)$	2.72	−0.25	−0.38	−2.15	0.005
$TX(C)$	3.08	1.64	3.81	−5.53	−0.010
TP	−2.96	−0.84	1.31	−3.34	−0.003
TN/B	−3.57	−1.00	0.93	−3.87	−0.003
PN/B + $X(B)\,X(C)$	1.38	−0.7	0.45	−1.96	0.005
N/B $X(B) + PX(C)$	−2.42	−0.66	−9.51	5.98	0.007

effect (from lower to higher level) of the involved factor or alias.

Weight increase, Δm, and thickness, t: the factor that has the greatest influence is the molar fraction of boron trichloride, $X(\mathrm{B})$. This is due to the very strong effect of chlorinated species on the acetylene pyrolysis efficiency [21] (pure acetylene gives low deposition rates in this temperature range).

The different hierarchy of the estimates for Δm and t could indicate that the density of the coatings does not remain constant, although the coatings always seem to be dense, smooth and of a metallic appearance (Fig. 3). But poor accuracy of the thinner coating thickness measurements is probably the main reason for this feature. At this time, no systematic and direct determination of the density has been made due to the very strong adhesion of the films to the substrate and to the low amounts available.

Coating composition: all the compositions exhibit an atomic ratio at % B/at % N greater than unity (Table III) which justifies the $\mathrm{C}_a(\mathrm{BN})_b\mathrm{B}_{1-a-b}$ formulation. It must be noticed that the compositions of coatings 16 and 5 are unreliable: the first one is very thin (ZAF correction program of the EPMA is not able to deal with the substrate contribution), and the second one exhibits a marqued insulator character which is incompatible with an accurate determination.

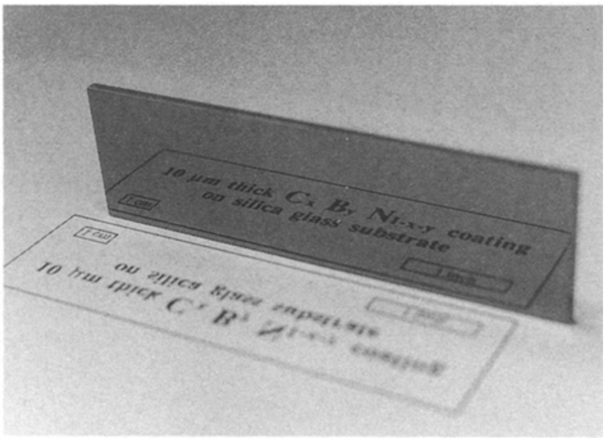

Figure 3 Photograph of a film.

TABLE III Atomic composition and B/N ratio of the deposits

	$\mathrm{C}_x\mathrm{B}_y\mathrm{N}_{1-x-y}$			
	x (at % C)	y (at % B)	$1-x-y$ (at % N)	$y/1-x-y$ (at % B/at % N)
1	42.6	34.6	22.8	1.52
2	76.8	20.5	2.7	7.58
3	65.6	27.0	7.4	3.64
4	80.3	19.7	0.0	
5	4.0	57.2	38.8	1.47
6	73.7	17.6	8.7	2.04
7	43.3	33.0	23.7	1.39
8	73.3	19.3	7.4	2.63
9	76.9	15.0	8.1	1.86
10	18.5	41.9	39.6	1.05
11	12.8	47.1	40.1	1.18
12	53.0	23.5	23.5	1.01
13	100.0	0.0	0.0	
14	75.9	18.9	5.2	3.63
15	78.6	16.3	5.1	3.17
16	48.6	50.3	1.1	45.73

In a first attempt, the $a(b)$ coefficient could be seen as an indicator of the "graphite (boron nitride) character" of the coating. Temperature is the main factor which influences the a coefficient, indicating the thermal activation of acetylene pyrolysis. Symmetrically, b is less temperature-dependent and the most important factor is the N/B parameter. These features both demonstrate how different are the two elementary kinetics involved in this process in terms of pyrolytic carbon and pyrolytic boron nitride codeposition.

Further discussion about the relative level of the estimates is difficult, owing to the very similar influence of all the parameters. None of them has little importance. The good aspect is that the experimental domain is judicious and enables a very wide composition diversity to be reached. This is illustrated in Fig. 4 where the different composition values are reported on a ternary C–B–N diagram. Not only experimental design results are reported but also previous and complementary ones. All the coatings can be described in the pseudo-ternary C–BN–"BC_3" part, "BC_3" being at this time the carbon-richest compound synthesized in the C–B system [4]. In addition, the experimental elemental composition of the inlet gas stream (leaving chlorine and hydrogen out of account) is represented in the white triangle. It would be interesting to determine out if the actual composition domain can be extended more extensively by making other choices of appropriate experimental conditions. Of special interest would be the extension to the "boron corner", in order to ascertain if the "BC_3" material is the limit beyond which a two-phase compound, including boron carbide, is synthesized.

The possibility of using the estimates of the experimental design as a predictive empirical model is clearly illustrated by the results of some complementary experiments. The parameter values were set in the middle of the above experimental domain. On the one hand, the experimental reliability for duplicated experiments is better than 98% (for the carbon content). On the other hand, the actual content is as much as

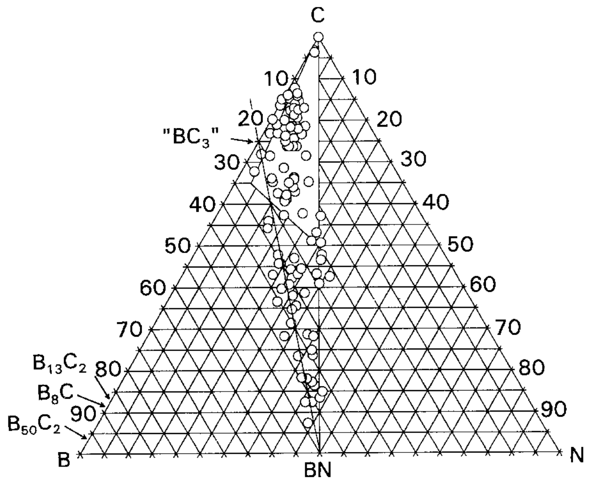

Figure 4 C–B–N composition diagram.

20% from the calculated one. This kind of model, a first-order one, is obviously inadequate to describe satisfactorily this complex chemical system which involves gaseous phase initiation. Further experiments and probably a change in the parameters set will be necessary to improve the model. In particular, the residence time notion [21] could be a parameter of great interest. This factor is defined as $\tau = A\,P\,T_0/F_0P_0T$. A is a factor depending on both the reactor geometry and the substrate position, P and T are the actual experimental pressure and temperature, P_0 and T_0 the standard pressure and temperature, and F_0 the total flow rate (measured at P_0 and T_0). τ involves P and T and it could be judicious to substitute (T, τ) for (P, T).

$d(0\,0\,2)$ spacing: all the "as-deposited" coatings exhibit a very simple X-ray diffraction pattern with an intense 0 0 2 peak and a rather small 0 0 4 one. This is

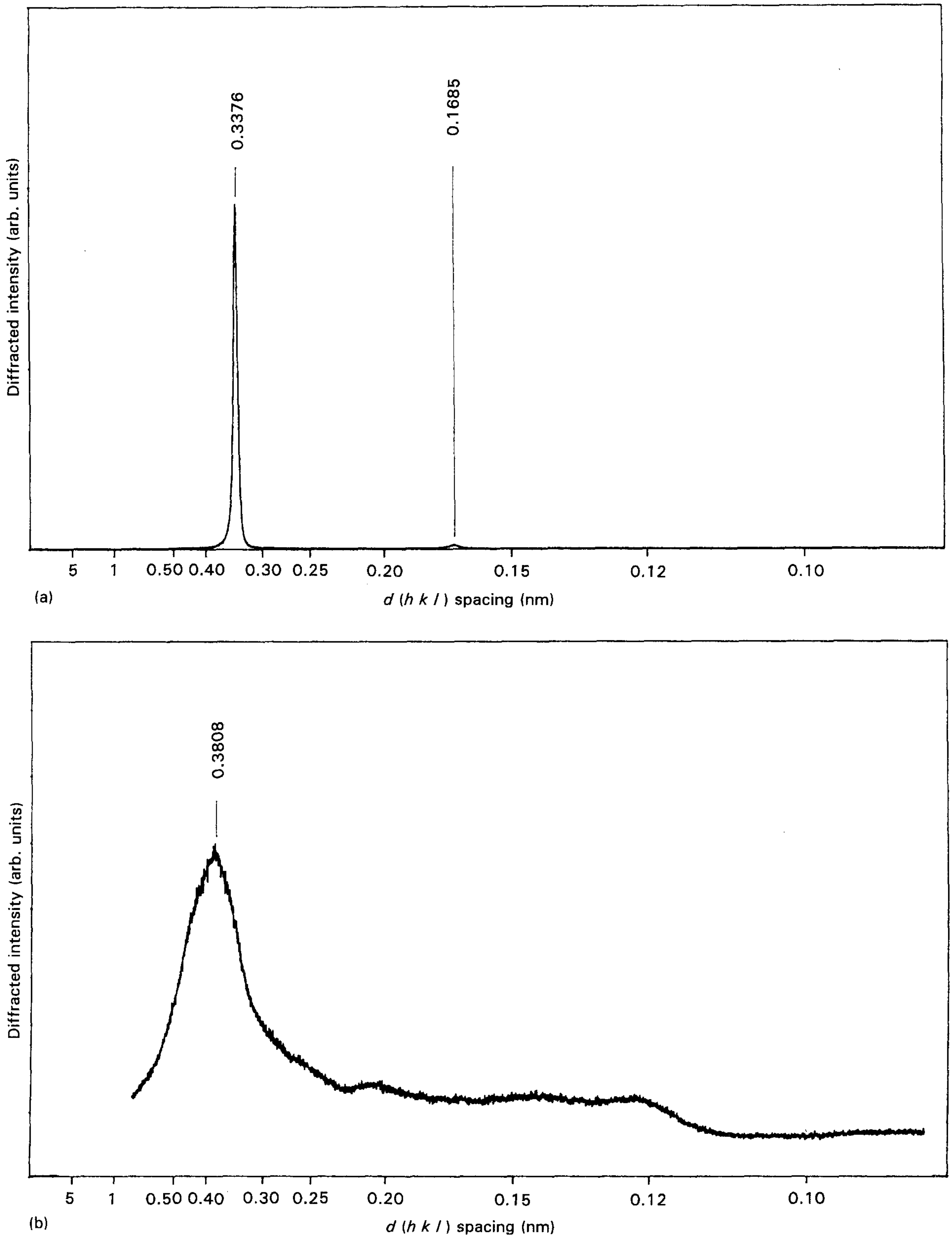

Figure 5 X-ray diffraction pattern of two characteristic samples, (a) a carbon-rich one (narrow 0 0 2 peak) and (b) a "BN"-rich one (wide 0 0 2 peak).

an indication of two features: the turbostratic character of the deposits and the very high level of texture, the sheets having an orientation mainly parallel to the substrate surface. Evidence for additional peaks due to a two-phase mixture (especially boron carbide) has never been observed.

The factors that have the greatest influence are temperature, T, and the interaction between temperature and molar fraction of acetylene, $TX(C)$. This can be summarized as follows: patterns can be classified into two characteristic types (Fig. 5); the first one having very thin full width at half maximum intensity (FWHM) is generally associated with the lower values of $d(0\,0\,2)$ and a high carbon content (a coefficient). Symmetrically, the second one associates wide FWHM, high values for $d(0\,0\,2)$ and high contents of boron nitride (b coefficient). Note that determination of the $d(0\,0\,2)$ spacing for high FWHM peaks cannot be accurate, because some coatings could almost be considered as amorphous ones.

5. Conclusions

The influence of experimental parameters on the chemical vapour deposition of C–B–N materials was investigated by means of the experimental design methodology. This phenomenological approach was chosen because in such complicated systems, the details of every relevant mechanism at work may never be known in a first step. The selected experimental domain leads to the synthesis of compounds, whose large variety of compositions are located inside the C–BN–"BC_3" ternary domain. Further experiments are necessary to make the model predictive from a composition point of view, but it is already noticeable that such a wide composition domain can be reached without the appearance of the most stable phases such as boron carbides. At a macroscopic scale, the coatings appear dense, smooth and of single phase, but at a nanometric scale, there is, at this time, no absolute evidence for the deposits to be a solid solution rather than a mixture of pyrolytic carbon and pyrolytic boron nitride.

Knowledge obtained about this process will now allow investigations of the electronic and magnetic properties, and also oxidation resistance of C–B–N compounds of well-defined compositions.

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