Regularities of pyrolytic boron nitride coating formation on a graphite matrix

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The kinetics and structure of chemical vapour-phase deposition of boron nitride ceramics on a graphite matrix from the mixture $BCl_3/NH_3/N_2$ have been investigated for a wide range of conditions (temperature 1300–2100 °C, pressure 130–2600 Pa, at varying partial pressures of the components). The growth-rate was found to vary non-linearly with the consumption rates of the reagents. The content of hexagonal components in the BN–ceramics rose, while the turbostrate microphase content diminished with temperature. The dependences of the concentrations of hexagonal, turbostratic and amorphous fractions in BN–ceramics on the reaction mixture composition and total pressure have been determined.

1. Introduction

The production of ceramic coatings and articles of pyrolytic boron nitride (PBN) by chemical vapour deposition (CVD) has been studied by number of researchers [1–13], who report the complexity of the process and PBN ceramics structure. However, it was felt that the phenomenon of PBN coating formation required some interdisciplinary detailed investigations in the fields of hydrodynamics and chemical kinetics, physics and chemistry of surface and phase transitions.

The CVD process is applied to the production of PBN crucibles. A (graphite) matrix of a desired shape heated to 1300–2000 °C (a "hot" substrate) is subjected to a "cold" flow of a vapour mixture (BCl_3–NH_3–N_2 or BCl_3–NH_3–H_2, BCl_3 being rather strongly diluted with other components). The complex chemical processes proceeding under such conditions result in a PBN layer growth on the matrix.

Articles of PBN ceramics (crucibles) manufactured by the CVD method from a BCl_3–NH_3–N_2 mixture have been shown [14] to consist of five structural varieties of hexagonal modifications of h-BN at a ratio dependent on the conditions of PBN ceramics synthesis.

The experimental data from a study of the effects of the synthesis conditions on the rate of PBN layer growth and the ratio of h-BN structural varieties are reported.
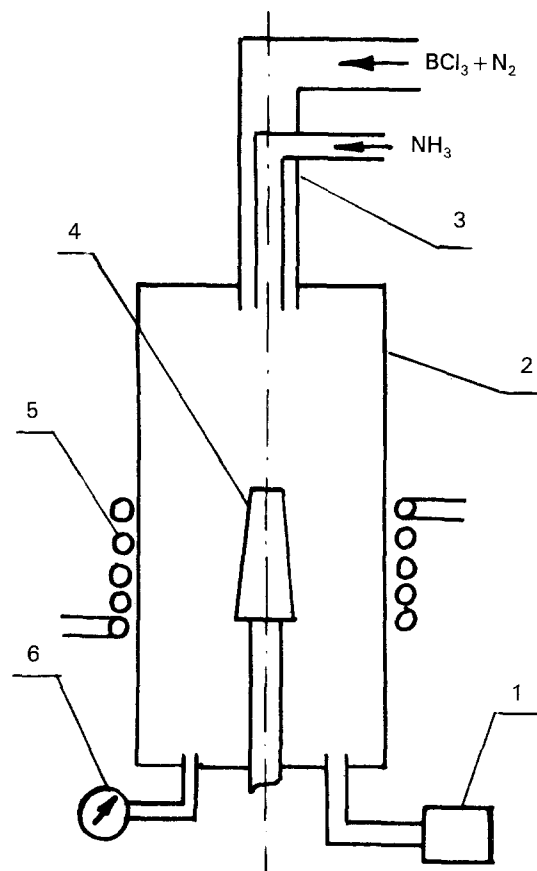

Figure 1 A schematic illustration of the apparatus for the production of articles of PBN. 1, Vacuum pump; 2, reactor; 3, gas outlet; 4, substrate (matrix); 5, vacuum meter.

2. Experimental procedure

2.1. Conditions required for the PBN coating synthesis

PBN crucibles of h-BN were produced in a special installation (see Fig. 1). Vapour mixtures of BCl_3, NH_3, and N_2 were prepared.

Heating of the graphite substrate to 2500 °C was performed by an inductive method using a 25 kW capacity generator at a frequency of 440 kHz. The substrate temperature was determined as a function of the power fed from the generator preliminarily calibrated against the standard material. The temperature was rated against the standard material. The temperature was registered using a pyrometer as a mean value of seven measurements at each point, the resulting accuracy being 30 °C.

The synthesis parameters were varied within the following ranges: matrix temperature, T_m, 1300–2100 °C; total pressure in the reactor, P_Σ, 1.3×10^2–2.6×10^3 Pa; rate of the NH_3 supply, $v(NH_3)$ (at an outlet pressure of 1.2×10^5 Pa), 2.0–6.4 l min^{-1}; rate of BCl_3 supply, $v(BCl_3)$ (at an outlet pressure of 1.5×10^4 Pa), 0.25–0.95 l min^{-1}.

One of the above parameters only was changed within each series, the others being maintained at their standard values, $T_m = 1990\,°C$, $P_\Sigma = 5.25 \times 10^2$ Pa, $v(NH_3) = 3.8$ l min^{-1}, $v(BCl_3) = 0.95$ l min^{-1}, $v(N_2) = 12.5$ l min^{-1} (at an outlet pressure of 4×10^4 Pa), $t_{syn} = 1$ h. On completion of synthesis, the thickness of the ceramic layer formed, its mean growth rate, u_g (mm h^{-1}), and the density of the ceramics synthesized, were measured.

2.2. IR spectroscopy

The procedure for recording the IR spectra was described in a previous paper [14].

In preliminary studies, the PBN ceramics microstructure was found to be uniform along the axis of a cylindrical crucible in its central part, though it changed noticeably near its edges (Fig. 2), which might be caused by turbulation of the vapour flow bend at the near-edge regions of the matrix and by changes in T_m due to distortions of the induction current configuration.

The material was shown to be structurally non-uniform in both axial and radial directions. Therefore, spectra were recorded on the samples taken from the middle part of the crucible, so that each sample contained all the layers in order to average radial inhomogeneities.
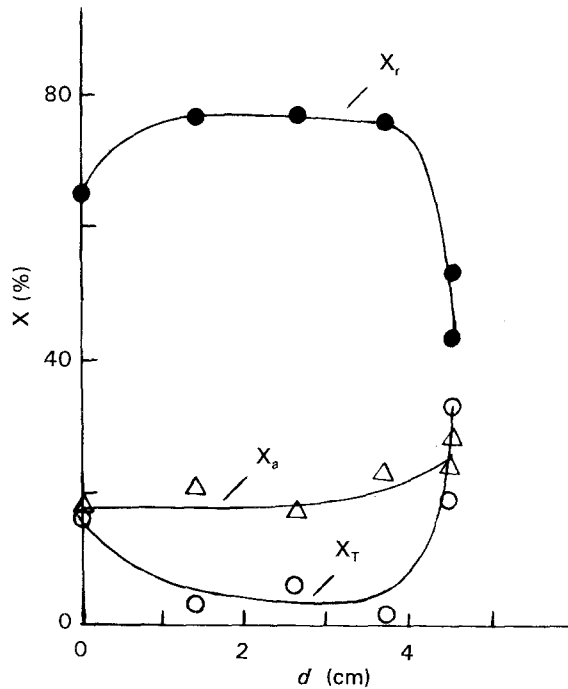

Figure 2 Distribution of the microphase composition along the PBN crucible (the coordinate zero corresponds to the upper part of the crucible). (●) X_h, (△) X_a, (○) X_t.

2.3. Determination of optimum ratios of structural components

Definition of structural modifications of h-BN proposed elsewhere [6–12] is, to a certain extent, conventional. Indeed, it seems impossible to distinguish between amorphous and turbostratic, turbostratic or partially regular modifications, because their classification is based on such parameters as the size of the crystal segment, L_a, interlayer distances, $d_{0\,0\,2}$, and concentration of sp^3-hybridized fragments. In a general case, all these parameters are gradually distributed.

Nevertheless, the IR spectra of the PBN ceramics contain a three-component band with relative maxima of the components at 770–785, 795–805, and 814–817 cm^{-1}, which correspond to $(a_1$-BN$)$ $+ (a_2$-BN$)$, t-BN, and (po-BN) $+$ (h-BN) structural modifications [14]. This is the evidence for the presence of three more or less individual microphases which are probably formed in different routes of the CVD process.

The intensities of the corresponding components may be used for quantitative determination of the content of each SC. It may be shown from IR spectroscopy theory that the integral extinction coefficient of the IR-active band is weakly dependent on L_a.

To verify the above statement, we consider a two-dimensional system of $N*N$-coupled oscillators in the normal coordinates of the elementary cell [15]. The integral extinction coefficient, ε_{int}^{km}, for the mode with the normal coordinate Q is

$$\varepsilon_{int}^{km} = \frac{A}{N^2}\left|\frac{\partial \mu}{\partial \theta_{km}}\right|^2 = \frac{A}{N^2}\left|\sum_{i,j=1}^{N}\frac{\partial \mu_{ij}}{\partial q_{ij}}\frac{\partial q_{ij}}{\partial \theta_{ij}}\right|^2 \quad (1)$$

where μ is a total dipole momentum, μ_{ij} is the dipole momentum of the (ij)th oscillator, q_{ij} is the local coordinate of the ij-oscillator, A is a constant, and N^2 the normalizing factor taking into account the number of oscillators.

When the (ij)th component of the (k, m)th eigenvector of normal vibrations is

$$l_{km}^{ij} = \frac{\partial q_{ij}}{\partial \theta_{km}}$$

$$= \frac{2}{N+1}\sin\frac{ik_n\pi}{N+1}\sin\frac{jk_m\pi}{N+1} \quad (2)$$

and the $\partial \mu_{ij}/\partial q_{ij}$ derivative is not i- and j-dependent because of the oscillator similarity, the following equation may be derived from Equation 1

$$\varepsilon_{int}^{km} = \frac{B}{N^2}\left|\sum_{i,j=1}^{N}\left(\frac{1}{N+I}\sin\frac{ikj}{N+I}\sin\frac{j\kappa\pi}{N+I}\right)\right|^2$$

$$= \frac{B}{N^2(N+I)^2}\sin\frac{k\pi}{2}ctg^2\frac{k\pi}{2(N+I)}\sin\frac{m\pi}{2}$$

$$\times ctg^2\frac{m\pi}{2(N+I)} \quad (3)$$

where B is a constant.

The intensity of the forbidden modes with even ks or ms is equal to zero according to Equation 3. The integral extinction coefficients of the band with odd

values of both k and m can be described by the following expression

$$\varepsilon_{ij}^{km} = B\left[ctg^2\frac{k\pi}{2(N+I)}ctg^2\frac{m\pi}{2(N+I)}\right]/[N^2(N+I)^2] \quad (4)$$

The value of the extinction coefficient of the main ε_{int}'' mode active in the IR spectrum is practically independent of N. The ε_{int}^{km} values of other harmonics diminish rapidly with the growth of N and at $N > 4$ they are more than an order lower than the ε_{int}'' value. Thus, the integral extinction coefficient of the band $v_\perp$ is seen to be independent of L_a.

ε_{int} is also likely to be weakly dependent on $d_{0\,0\,2}$, which may vary within a rather narrow range, hence the dielectric parameters of the absorbing centre (in particular, the $\partial\mu_{ij}/\partial q_{ij}$ value) are mainly determined by intralayer interactions. In this case, relative content of a particular structural variety of a layered BN may be considered to be proportional to the integral intensity of the corresponding component of the IR spectrum.

The integral intensities of the spectral bands corresponding to $(a_1\text{-BN}) + (a_2\text{-BN}) - X_a, (\text{t-BN}) - X_t$, and $(\text{po-BN}) + (\text{h-BN}) - X_h$, the superposition of which precisely describes the $v_\perp$ total contour, were used in further determination of the relative content of corresponding structural components.

The least squares method was used for the $v_\perp$ approximation by the bands preliminary found from the IR spectra of model samples of a_1-BN, t-BN, and h-BN.

3. Results and discussion
3.1. Macrokinetic regularities of the PBN layer formation

Under continuous flow conditions near the matrix surface there may arise a narrow zone (a boundary layer) [16], in which major chemical and deposition processes take place [13]. The temperature near the layer is close to that of T_m, its thickness, δ, is of a $1/\text{Re}$ order [17], where $\text{Re} = (\rho vl)/\mu$ is the Reynolds number (ρ is the vapour mixture density, v the linear rate of the vapour mixture against the matrix, μ the dynamic

Figure 3 u_g plotted against $v(\text{BCl}_3)$. $T_m = 1950\,°C$; $v_{NH_3} = 3.81\,\text{min}^{-1}$; $v_{N_2} = 12.51\,\text{min}^{-1}$; $P_\Sigma = 5.25 \times 10^2\,\text{Pa}$; $\tau_c = 1\,\text{h}$. (———) Calculated data.

viscosity of the matrix, and $l \simeq 10\,\text{cm}$ is the length of the matrix over which the vapour mixture flowed.

Thus, the boundary layer can be considered as an open system, which is fed (the rate of gaseous product removal being v_2), assuming that all processes involved in the PBN coating formation proceed inside the δ-layer of $V = S\int_0^1 l\,dl$, where S is the matrix square. The PAN layer growth results from a sequence of processes proceeding in the δ-layer and on the interface, e.g. the formation of products as the result of chemical reactions in the δ-layer, their diffusion (transfer) to the interface, their adsorption (trapping) by the matrix surface, and chemical processes on the surface of the matrix causing PBN layer formation.

In this case, the change in the molar number of the first component of the vapour–gas mixture in the δ-layer volume can be written as [18]

$$\frac{\partial(C_iV)}{\partial t} = C_{io}v_1 + W_{io}V - W_{ie}V - C_iv_2 \quad (5)$$

where C_{io}, C_i are the i-component concentrations in the reaction mixture fed on and escaped, respectively; $(C_{io}-C_i)$ is the amount of the i-component consumed during the product formation; W_{io}, W_{ie} are the rates of the i-component formation and consumption, respectively. Because the BCl_3 portion in the mixture is small, the changes in the volume after chemical reaction may be neglected and considered to be caused by the difference in v_1 and v_2. Hence

$$\frac{\partial V}{\partial t} = v_1 - v_2$$

and consequently

$$\frac{\partial(C_iV)}{\partial t} = V\frac{\partial C_i}{\partial t} + C_i\frac{\partial V}{\partial t}$$

$$= V\frac{\partial C_i}{\partial t} + C_i(v_1 - v_2) \quad (6)$$

Then

$$\frac{\partial C_i}{\partial t} = W_{io} - W_{ie} + \frac{v_1}{V}(C_{io} - C_i) \quad (7)$$

Under conditions of a steady-state regime $(\partial C/\partial t = 0)$

$$W_{ie} = W_{io} + (v_1/V)(C_{io} - C_i) \quad (8)$$

Because the i-component consumption is caused by the deposition of the product on to the matrix surface

$$u_g \simeq W_{ie} = W_{io} + (v_1/V)(C_{io} - C_i) \quad (9)$$

Thus, u_g may be affected by v_1 (the rate of the component supply), C_{io} (the component concentration in the fed-on flow), and W_{io} (the rate of the product formation in the gas phase).

The increase in the fitting rate of the BCl_3 (Fig. 3) and NH_3 (Fig. 4) results in an increase in the rate of PBN layer growth $u_g[v(\text{BCl}_3)]$ and $u_g[v(\text{NH}_3)]$ dependences are S-shaped and may be satisfactorily described by empirical equations

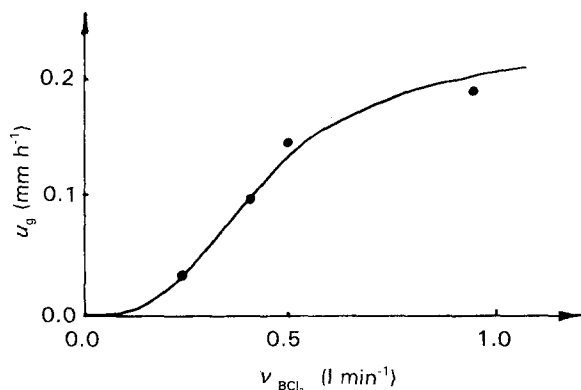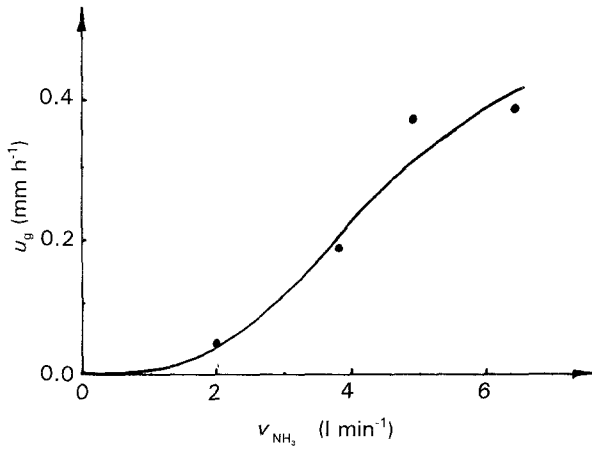$$u_g = \frac{2.98v^3(\text{BCl}_3)}{1 + 14.14v^3(\text{BCl}_3)} \quad (10)$$

Figure 4 u_g plotted versus $v(NH_3)$. $T_m = 1950\,°C$; $v_{BCl_3} = 3.8\,1\,min^{-1}$; $v_{N_2} = 12.5\,1\,min^{-1}$; $P_\Sigma = 5.25 \times 10^2$ Pa; $\tau_c = 1$ h. (———) Calculated data.

$$u_g = \frac{5.95 \times 10^{-3}v^3(NH_3)}{1 + 1.01 \times 10^{-7}v^3(NH_3)} \quad (11)$$

At constant $v(BCl_3)$, $v(NH_3)$, $v(N_2)$ and low P_Σ, the increase in the latter (the change in W_{io}, C_0, C_{ic}, respectively) enhances u_g, which remains practically constant from above $P_\Sigma = 9 \times 10^2$ Pa (Table I).

Deposition of the products of chemical conversions in the δ-layer on to the matrix surface is caused by the flow diffusion to the surface of the matrix and their trapping there. If $\delta^2/D_i \gg \delta/\varepsilon_i u_i$, where D_i, ε_i, u_i are the diffusion coefficients, the probability of entrapping by the matrix surface, and the average rate of i-particle motion, respectively, the deposition proceeds in the diffusion regime. In the case when $\delta^2/D_i \ll \delta/\varepsilon_i u_i$, the process runs in the kinetic regime.

In the diffusion regime, the PBN layer growth should depend linearly on the total pressure inside the reactor; however, the data in Table I do not indicate that. At the constant pressure, u_g should have increased linearly with $v(BCl_3)$ and $v(NH_3)$, though it was not observed (Figs 3, 4). The combination of these data evinces the process of PBN layer formation to proceed in the kinetic regime (or in an intermediate kinetic diffusion region). This is probably the consequence of low P_Σ. The u_g value is weakly T_m-dependent (Table II).

An increase in u_g with increasing T_m is observed up to $1500\,°C$, above which u_g is T_m-independent. Such a peculiar dependence of u_g is T_m leads to the conclusion that if the process of PBN layer formation proceeds in the kinetic regime, the probability, ε_i, of entrapping the gas-phase particles, which form the layer, is practically independent of T_m above $1500\,°C$.

Thus, PBN coating formation under the conditions of the experiment is greatly affected by $v(BCl_3)$ and $v(NH_3)$ values, the influence of P_Σ and T_m being observed in regions of their low values.

3.2. The synthesis-dependent ratios of SC in h-BN

The increase in T_m is seen to cause an increase in X_h and a decrease in X_t (Fig. 5). At the same time, $X(T)$ is of a complicated character, a_1-BN and a_2-BN being predominantly formed at temperatures below $1600\,°C$ and above $1900\,°C$, respectively.

The dependence of the SC content on P_Σ (Fig. 6) is in qualitative agreement with the data Matsuda *et al.* [1] (the review gives the most complete presentation
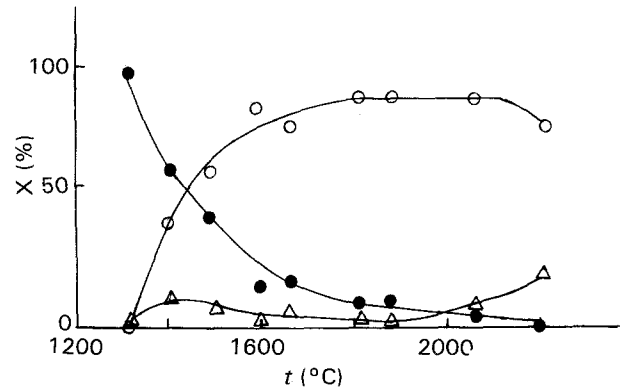

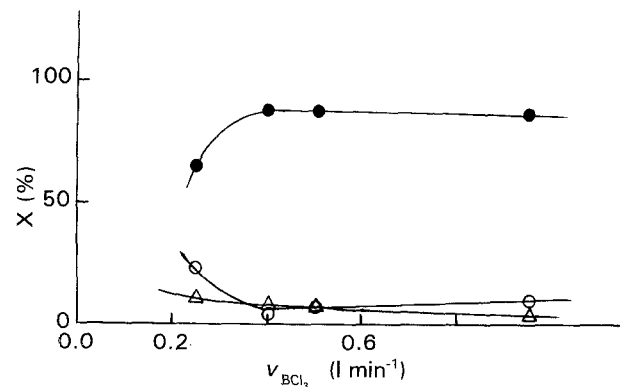*Figure 5* The dependence of the (O) X_h, (●) X_t, and (△) X_a structural components on T_m.

Figure 6 The dependence of the (●) X_h, (O) X_t, and (△) X_a structural components on v_{BCl_3}.

TABLE I The effect of P_Σ on u_g ($T = 1950\,°C$, $v(BCl_3) = 0.95\,1\,min^{-1}$, $v(NH_3) = 3.8\,1\,min^{-1}$, $v(N_2) = 12.5\,1\,min^{-1}$, $\tau_c = 1$ h)

P_Σ (Pa)				
1.3×10^2	5.3×10^2	9.2×10^2	1.3×10^3	2.5×10^3
u_g(mm h^{-1}) 0.23	0.18	0.32	0.35	0.32

TABLE II The effect of T_m on the u_g ($v(BCl_3) = 0.95\,1\,min^{-1}$, $v(NH_3) = 3.8\,1\,min^{-1}$, $v(N_2) = 12.5\,1\,min^{-1}$, $\tau_c = 1$ h, $P_\Sigma = 5.3 \times 10^2$ Pa)

$T(°C)$								
1330	1410	1490	1590	1660	1730	1810	1880	1950
u_g(mm h^{-1}) 0.09	0.14	0.19	0.175	0.185	0.180	0.175	0.170	0.180

of works on the CVD method carried out by 1984). However, when account is taken of the smooth shape of those dependences, P_Σ is hardly recommendable as a convenient parameter for plotting of the phase diagram.

The value of X_h also increases with BCl_3 concentration in the vapour mixture and decreases with decreasing NH_3 concentration (Figs 7, 8), an increase in the concentration of NH_3 (which is always in excess compared with BCl_3) resulting in a simultaneous increase in both the X_h value (as well as X_a) and the N–H bond content in the ceramics. The latter is detected by the consumption in the region of 3000–3500 cm^{-1}. However, the question of whether the N–H bond belongs to the turbostratic microphase is still obscure.

Figure 7 The dependence of the (●) X_h, (○) X_t, and (△) X_a structural components on v_{NH_3}.

3.3. Possible routes of interaction in the BCl_3–NH_3–H_2 system

Thermodynamic analysis of the BCl_3–H_2–N_2 [13] and BCl_3–NH_3–H_2 [19] systems showed that the BN-layer growth at 1300–2200 °C was realized via the BCl particle diffusion to the interface [13], their adsorption and dissociation on the surface being followed by
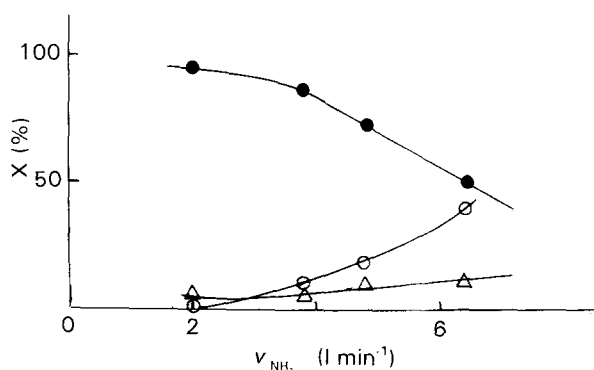
structural modifications in the ceramics synthesized, in particular in the case of the BCl_3–NH_3 mixture.

At the same time, in our opinion, the possibility of interaction of BCl_3, NH_3 and their dissociation products at low temperatures and the formation of cyclochloroboronazines [20–25] which are applied to the PBN production [16], are not taken into account. Cyclization may be preceded by the formation of a linear trimer [24]

$$BCl_{3(g)} + NH_{3(g)} \xrightarrow{-HCl} BCl_2-NH_2 \xrightarrow{} \frac{1}{3}(BCl_2NH_2)_3 \xrightarrow{-HCl} \qquad (12)$$
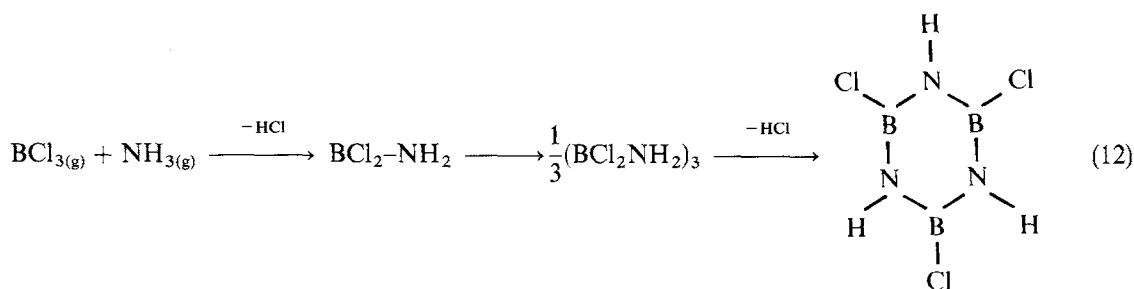
the B,N-adatoms and BN-admolecules incorporation into the BN matrix. Thus, the presence of vapour phase in the δ-layer was attributed to the establishment of a thermodynamic equilibrium, followed by the escape of thermodynamically equilibrated particles formed, to the matrix surface. However, such a mechanism of BN-layer formation does not elucidate the existence of the diversity of the h-BN

Taking into account a low amount of BCl_3 (much lower than that of NH_3 and ~ 30-fold less in our case) and the total pressure of the reacting vapour mixture of the order of 10^2–10^3 Pa, the above processes may be expected to proceed during the initial stage of mixing in the absence of BCl_3.

Cyclic boron–nitrogen fragments formed may undergo polymerization to yield the fragments of the h–BN structures, when reaching the high-temperature zone of the δ-layer [26].
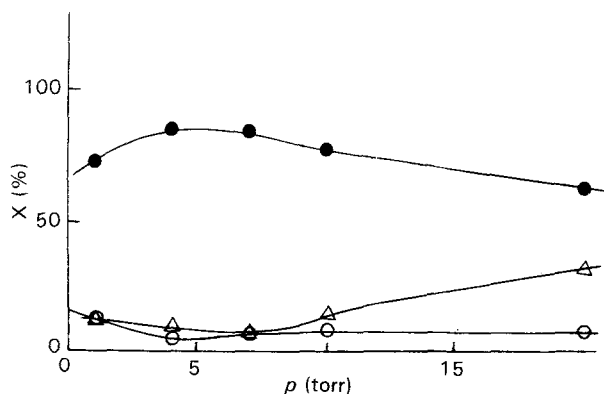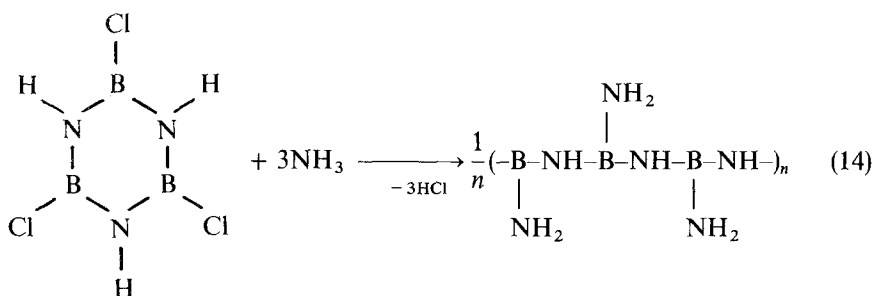

$$2B_3N_3H_3Cl_3 \xrightarrow[-HCl]{} \xrightarrow[-2HCl]{+B_3N_3H_3Cl_3} \qquad (13)$$

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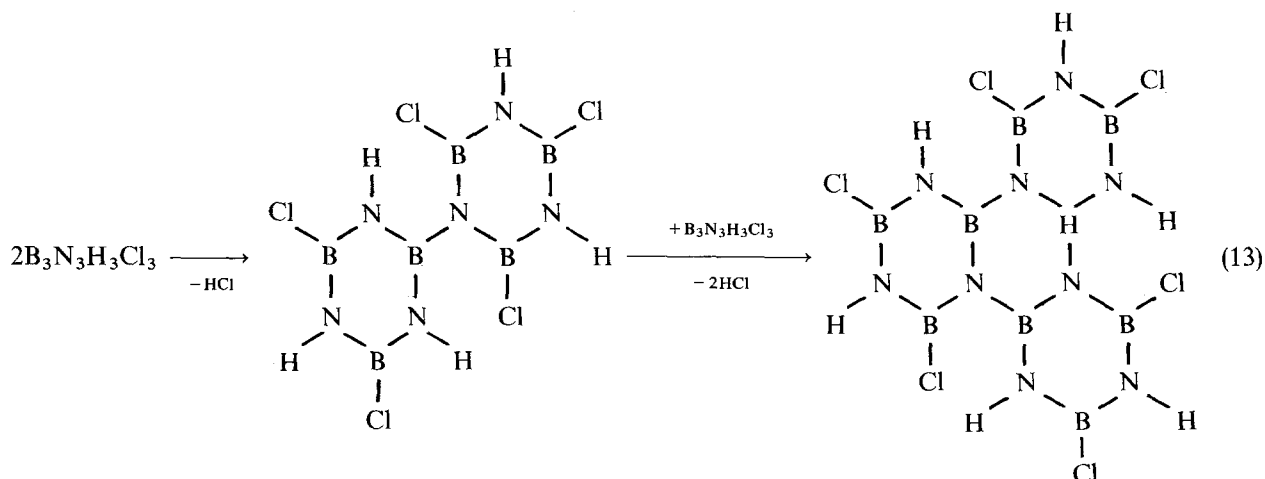
Figure 8 The dependence of the (●) X_h, (△) X_t, and (○) X_a structural components on P_Σ.

Similarly to other reports [27–29], simultaneous destruction of the boron–nitrogen ring may take place before the formation of both BCl and NH fragments and those of polymer structures (due to the NH_3 excess in the mixture).

Cyclic and linear B–N fragments precipitate on to the matrix and form various structural h-BN modifications of the PBN ceramics.

The presence of the B–N–H polymer fragments in the PBN ceramics may be the cause for the appearance of an absorption band in the region of the N–H valency oscillations (3000–3500 cm^{-1}) of the IR spectra with increase in the NH_3 concentration in the vapour mixture (simultaneously with that in the t- and a-BN contents).

The analysis of the kinetic peculiarities and the scheme of chemical conversion will be the subject of a subsequent communication [30].

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