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Thermodynamic analysis of the refining of technical boron nitride

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The efficiency of the process of refining technical boron nitride was assessed based on calculations of the chemical equilibrium in the B–N–O–C–Cl–H system. Three refining mixtures, $CCl_4 + H_2$, $CCl_4 + NH_3$ and $CHCl_3 + NH_3$, were considered. The analysis indicates that the use of ammonia-containing mixtures is more convenient, a lower residual oxygen content, lower contamination of the product by carbon and a better overall boron balance emerging. The calculations of the equilibrium composition of the solid phase enabled suitable technological conditions of the refining process (temperature and starting composition of the gaseous phase) to be established. The calculated results are compared with experimental data, and some observed differences are discussed.

1. Introduction

Boron nitride ceramics are finding ever-extending application in technical practice. Parameters of products from sintered boron nitride are determined to a great extent by the physical and chemical properties of the starting raw material powder, the residual oxygen content playing a major role. Reduction in the oxygen content to a tolerable limit can be achieved in several ways. A method based on reductive chlorination has been suggested by us previously [1]; in this procedure, oxygen is removed with a gaseous mixture of a chloro derivative of methane (CCl_4 or $CHCl_3$) with hydrogen or ammonia. The result of this refining process, i.e. changes in residual oxygen and carbon contents of the powder and the overall boron balance, is affected particularly by the refining temperature, starting composition and total amount of gaseous phase.

For an a priori assessment of these effects, a detailed thermodynamic analysis of the B–N–O–C–Cl–H system is made in this work, and based on this, suitable technological conditions of the refining process are suggested. The calculated results are compared with some experimental data.

2. Calculation of Chemical Equilibrium in the B–N–O–C–Cl–H System

To our knowledge, results of equilibrium calculations of this system have not so far been published. Several papers, however, exist dealing with some subsystems, e.g. B–Cl–H [2–4] B–C–Cl–H [5] and B–N–Cl–H [4, 6], under conditions of deposition of solid B, B_4C or BN from the gaseous phase.

2.1. Description of the system

It is assumed for the calculations that all oxygen present in the solid phase is bonded in the form of boron(III) oxide. Condensed B_2O_3, which melts at 723 K, and solid boron nitride are regarded as two individual mutually immiscible phases. Reacting with $CCl_4 + H_2$, $CCl_4 + NH_3$ or $CHCl_3 + NH_3$ gases, oxygen is transferred from B_2O_3 to the gaseous phase as carbon monoxide. The boron liberated also passes into the gaseous phase in the chloride form; if ammonia is used, nitridation associated with the formation of solid BN takes place. A number of additional chemical reactions can also occur depending on temperature and on the starting composition of the gaseous phase. Therefore, a total of 30 gaseous substances, selected based on results of equilibrium calculations for the above subsystems and on our experience gained from calculations of chemical equilibria of similar systems [7], are included (Table I). The possibility of formation of elemental carbon (graphite), boron and boron carbide, B_4C, is also taken into account. Again, all of these substances are regarded as single-component phases.

2.2. Calculation method and input thermodynamic data

The modified White–Johnson–Dantzig method was used for the calculation of the chemical equilibrium; in this method, the point of absolute minimum of the Gibbs energy of the system is sought on a set of points satisfying the mass balance conditions. The computation program enables any number of single-component condensed phases to be included, in addition to the gaseous phase. In the starting stage of the calculation, a system comprising the gaseous phase and two initial single-component condensed phases, namely B_2O_3(l) and BN (s), was treated. After determining the equilibrium state of this system, the Kuhn–

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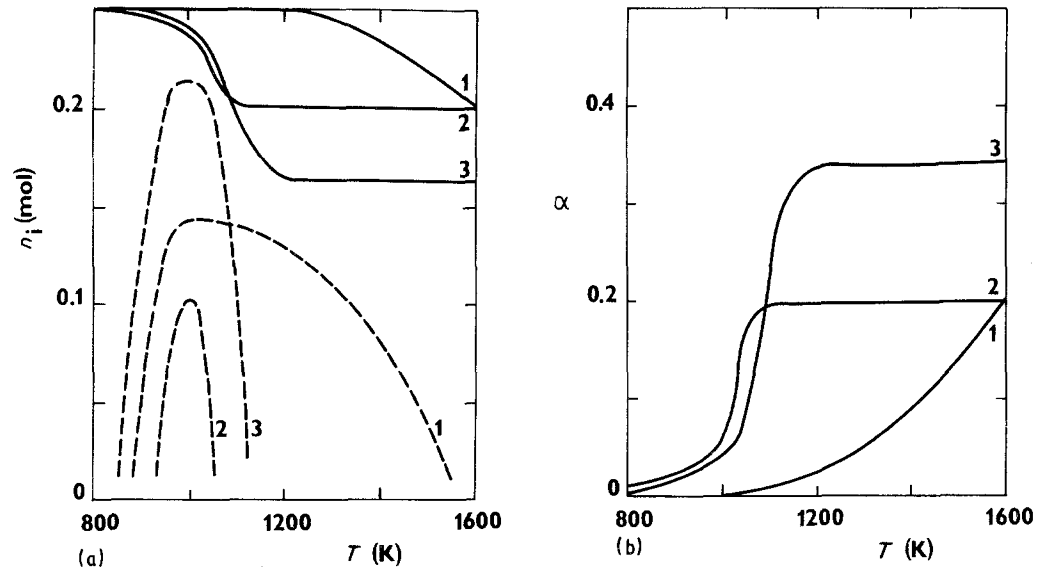

Figure 1 Temperature dependences of the equilibrium amounts of boron (III) oxide and carbon (a) and of the degree of conversion of the B_2O_3 initially present (b). $n_g^0 = 1.25$ mol; 1, CCl_4($x = 0.116$) + H_2; 2, CCl_4($x = 0.116$) + NH_3; 3, $CHCl_3$($x = 0.205$) + NH_3. (——) B_2O_3; (– – –) carbon.

Tucker conditions are applied to ascertain whether formation of a small quantity of some other condensed phase (in our case C, B_4C or B) is associated with a decrease in the total Gibbs energy of the system. If this is the case, this substance is included in the system treated and the calculation is repeated. The calculation is terminated if no additional decrease in the Gibbs energy of the system can be achieved by incorporation of an additional phase. The calculation procedures are described in detail by Smith and Missen [8] and Holub and Voňka [9].

The input thermodynamic data are standard molar Gibbs energies of the individual substances, $G_i^0(T)$, which are available for all substances considered [10–12] (Table I).

2.3. Results of calculations

The calculations were performed for 200 different starting conditions over the temperature region 800 to 1600 K at a pressure of 101.3 kPa. The starting composition of the system was chosen so as to enable the results to be compared with some of our experimental data [1]. The starting amount of technical boron nitride powder, which contained 82.5 wt % BN and 17.5 wt % B_2O_3, was invariably 100 g, hence, $n_{BN}^0 = 3.324$ mol and $n_{B_2O_3}^0 = 0.251$ mol. The total admitted gas volume was 30, 60, 90, 150 or 240 l at 293.15 K and 101.3 kPa, which corresponds to the total amounts of initial gas mixture $n_g^0 = 1.25$, 2.5, 3.75, 6.25 and 10 mol, respectively. The starting mole fraction of the methane chloro derivate in the gas mixture was varied over the region $x^0 = 0.05$ to 0.50. Some calculations were performed for starting mole fractions $x_{CCl_4}^0 = 0.116$ or $x_{CHCl_3}^0 = 0.205$, which relate to the saturated vapour pressures of these substances at 293.15 K [13] and correspond to concentrations used in our experiments.

TABLE I Chemical species included in equilibrium calculations (along with references to thermodynamic data sources)

Species	Ref.	Species	Ref.	Species	Ref.
BCl_3(g)	[11]	BOH(g)	[12]	CH_4(g)	[11]
BCl_2(g)	[11]	B_2O_3(g)	[12]	C_2H_4(g)	[12]
BCl(g)	[11]	HCl(g)	[11]	C_2H_2(g)	[11]
B_2Cl_4(g)	[12]	H_2O(g)	[11]	HCN(g)	[12]
BH_3(g)	[12]	H_2(g)	[11]	N_2(g)	[11]
BH_2(g)	[12]	O_2(g)	[11]	NH_3(g)	[11]
BH(g)	[12]	Cl(g)	[11]	BN(s)	[12]
B_2H_6(g)	[12]	CO(g)	[11]	B_2O_3(l)	[11]
$BHCl_2$(g)	[12]	CO_2(g)	[11]	B(s)	[11]
BH_2Cl(g)	[12]	$COCl_2$(g)	[11]	B_4C(s)	[11]
BHCl(g)	[12]	CCl_4(g)	[11]	C(s)	[11]
BOCl(g)	[11]	$CHCl_3$(g)	[12]		

2.3.1. Dependence of equilibrium composition on temperature

The dependence of the equilibrium amounts of B_2O_3 (l) and carbon on temperature, for two different total initial amounts of the gaseous phase ($n_g^0 = 1.25$ and 6.25 mol) and a constant initial concentration of methane chloro derivative, are shown in Figs 1 and 2, respectively. The temperature dependences of the degree of conversion of the boron(III) oxide initially present, $\alpha = (n_{B_2O_3}^0 - n_{B_2O_3})/n_{B_2O_3}^0$ where $n_{B_2O_3}^0$ and $n_{B_2O_3}$ are the initial and equilibrium amounts of B_2O_3 substance, respectively, are also included. The following conclusions can be drawn from these dependences and the calculated composition of the gaseous phase.

(a) The equilibrium amount of B_2O_3 decreases invariably with increasing temperature. Replacement of hydrogen by ammonia brings about a substantial increase in the degree of conversion of the initial boron (III) oxide as well as an improvement in the overall boron balance, because with the CCl_4 or $CHCl_3$ concentrations considered, virtually all boron from the reacted B_2O_3 is transformed into solid BN. The degree of conversion of the B_2O_3 initially present is practically determined by the possibility of formation of carbon monoxide, which under the conditions used is the thermodynamically most stable oxygen-containing gaseous substance. This is well demonstrated by Fig. 1. In this case, $n_{CCl_4}^0 = 0.1447$ mol, and no more than the same amount of CO can be formed.

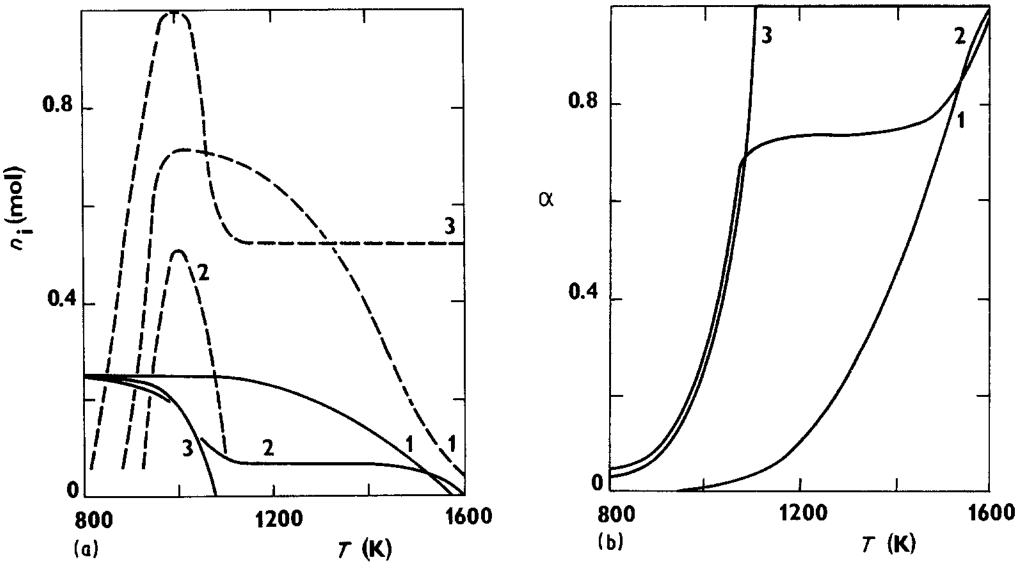

Figure 2 Temperature dependences of the equilibrium amounts of boron (III) oxide and carbon (a) and of the degree of conversion of the B_2O_3 initially present (b). n_g^0 = 6.25 mol; 1, CCl_4 (x = 0.116) + H_2; 2, CCl_4 (x = 0.116) + NH_3; 3, $CHCl_3$ (x = 0.205) + NH_3. (——) B_2O_3; (- - -) carbon.

Thereby, 0.1447 mol oxygen atoms is transferred into the gaseous phase, which corresponds to a loss of 0.048 mol B_2O_3 and an approximately 19% degree of conversion. The maximum values obtained based on equilibrium calculations are 20% for the CCl_4 + NH_3 system and 20.4% for the CCl_4 + H_2 system.

(b) Simultaneous with the reaction of B_2O_3, formation of solid carbon takes place; its equilibrium amount depends on temperature, starting composition and total amount of gaseous phase. For all systems (CCl_4 + H_2, CCl_4 + NH_3, $CHCl_3$ + NH_3), the calculated temperature dependences exhibit a maximum in the 1000 K range, this maximum being very sharp for the ammonia-containing systems.

(c) The equilibrium composition of the gaseous phase is strongly temperature-dependent. For the CCl_4 + H_2 system at low temperatures (800 to 1000 K), the dominant components of the gaseous phase are BCl_3, CH_4, CO, H_2O, H_2 and HCl; N_2 and NH_3 are also present if hydrogen is replaced by ammonia. The number of substances present in non-negligible quantities increased with increasing temperature. At 1600 K, the gaseous phase contains nearly 20 substances whose mole fraction is higher than 10^{-6}. Oxygen in the gaseous phase is bonded mainly in the form of CO; boron in the form of BCl_3, $BHCl_2$ and BOCl. In systems where NH_3 is the entering substance and the initial concentrations of CCl_4 or $CHCl_3$ are lower, boron is virtually absent from the gaseous phase, being bonded in the solid phase as BN. For the starting methane chloro derivative concentrations considered by us, the gaseous B_2Cl_4, BH_3, BH_2, BH, B_2H_6, C_2H_2, $COCl_2$ and O_2, whose mole fractions are below 10^{-8} over the entire temperature region, could be ignored. An example of the equilibrium composition of the gaseous phase at a temperature of 1200 K is given in Table II.

(d) Solid B and B_4C never form in the conditions used.

2.3.2. Dependence of equilibrium composition on starting concentration of methane chloro derivative

The dependences of the equilibrium amounts of B_2O_3 (l) and carbon and of the degree of conversion of the boron(III) oxide initially present on the starting concentration of CCl_4 in mixtures with hydrogen or ammonia are plotted in Fig. 3 for a temperature of

TABLE II Equilibrium composition of the gaseous phase of the B–N–O–C–Cl–H system at 1200 K for the total starting amount of gaseous phase n_g^0 = 1.25 mol (only species whose mole fraction x is higher than 1 × 10^{-6} are included)

Species	x_i		
	CCl_4(x = 0.116) + H_2	CCl_4(x = 0.116) + NH_3	$CHCl_3$(x = 0.205) + NH_3
BCl_3	7.20 × 10^{-3}	1.79 × 10^{-5}	5.22 × 10^{-5}
$BHCl_2$	1.25 × 10^{-3}		
BOCl	7.24 × 10^{-6}		1.40 × 10^{-6}
CH_4	1.74 × 10^{-4}	3.53 × 10^{-5}	5.05 × 10^{-5}
CO	1.09 × 10^{-2}	5.56 × 10^{-2}	9.56 × 10^{-2}
CO_2	2.23 × 10^{-6}	2.28 × 10^{-4}	3.63 × 10^{-4}
H_2O	2.98 × 10^{-5}	5.31 × 10^{-4}	4.31 × 10^{-4}
H_2	5.91 × 10^{-1}	5.26 × 10^{-1}	4.62 × 10^{-1}
HCl	3.91 × 10^{-1}	2.23 × 10^{-1}	2.88 × 10^{-1}
NH_3		2.40 × 10^{-6}	1.76 × 10^{-6}
N_2	2.43 × 10^{-5}	1.94 × 10^{-1}	1.54 × 10^{-1}
HCN		3.42 × 10^{-6}	5.30 × 10^{-6}
n_g(mol)	1.402	2.590	2.664

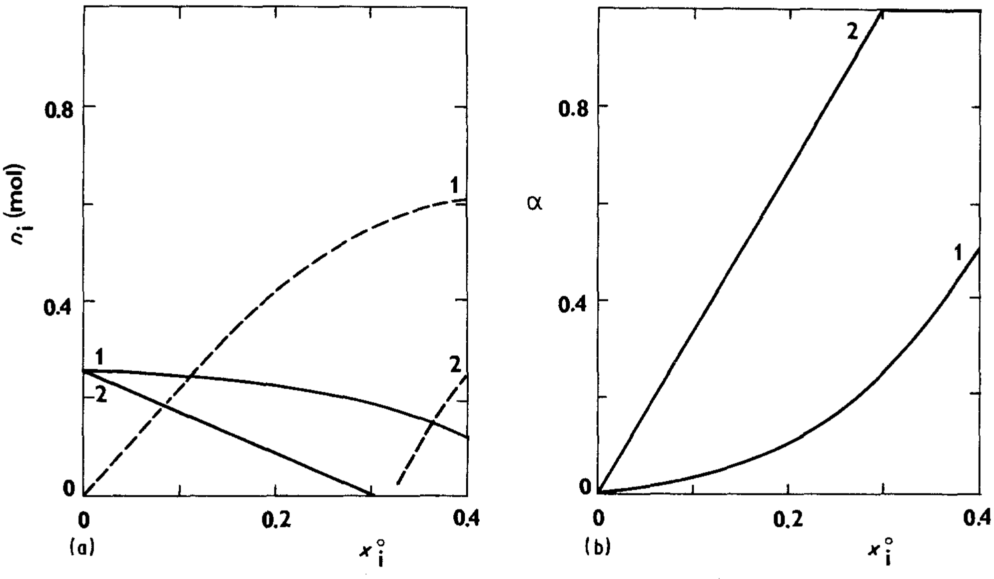

Figure 3 Dependences of the equilibrium amounts of boron (III) oxide and carbon (a) and of the degree of conversion of B_2O_3 initially present (b) on the starting concentration of CCl_4. $n_g^0 = 2.50$ mol; $T = 1200$ K; 1, $CCl_4 + H_2$; 2, $CCl_4 + NH_3$. (——) B_2O_3; (- - -) carbon.

1200 K. The calculated data for the $CHCl_3 + NH_3$ system are virtually identical with those for the $CCl_4 + NH_3$ system, and are not given. The degree of conversion of B_2O_3 increases with increasing starting concentrations of CCl_4 for both the $CCl_4 + NH_3$ and $CCl_4 + H_2$ mixtures and is higher for the former than for the latter. The amount of carbon formed also increases with increasing starting concentration of CCl_4. While in the case of $CCl_4 + H_2$, carbon starts to form even at very low starting concentrations of CCl_4, in the case of $CCl_4 + NH_3$, $x_{CCl_4}^0 > 0.3$ is required. For the latter case of $x_{CCl_4}^0 < 0.3$, virtually all boron from the reacted B_2O_3 is transformed into solid BN; at higher concentrations of CCl_4, BN reacts to give gaseous substances, particularly BCl_3 and N_2. Reaction of the boron nitride initially present with CCl_4 also takes place in the case of $CCl_4 + H_2$ systems, even at an initial concentration $x_{CCl_4}^0 = 0.20$; at $x_{CCl_4}^0 = 0.50$, the loss of solid BN is 13.9% of the initial quantity.

2.3.3. Dependence of equilibrium composition on total initial amount of gaseous phase

Fig. 4 shows the dependences of equilibrium amounts of B_2O_3 (l) and carbon and of the degree of conversion of the boron (III) oxide initially present on the total starting amount of gaseous phase at a temperature of 1200 K. Again, the data are given only for the $CCl_4 + H_2$ and $CCl_4 + NH_3$ systems, replacement of CCl_4 by $CHCl_3$ being accompanied by negligible change in the calculated equilibrium composition at this temperature. The equilibrium amount of boron (III) oxide decreases with increasing starting amount of gaseous phase, the refining efficiency again being higher if ammonia is used. In this case, the B_2O_3 initially present reacts completely at a total starting amount of gaseous phase $n_g^0 = 3.75$ mol ($x_{CCl_4}^0 = 0.20$), all boron from this oxide being transformed to solid BN. The amount of carbon formed increases with increasing starting amount of gaseous phase, and

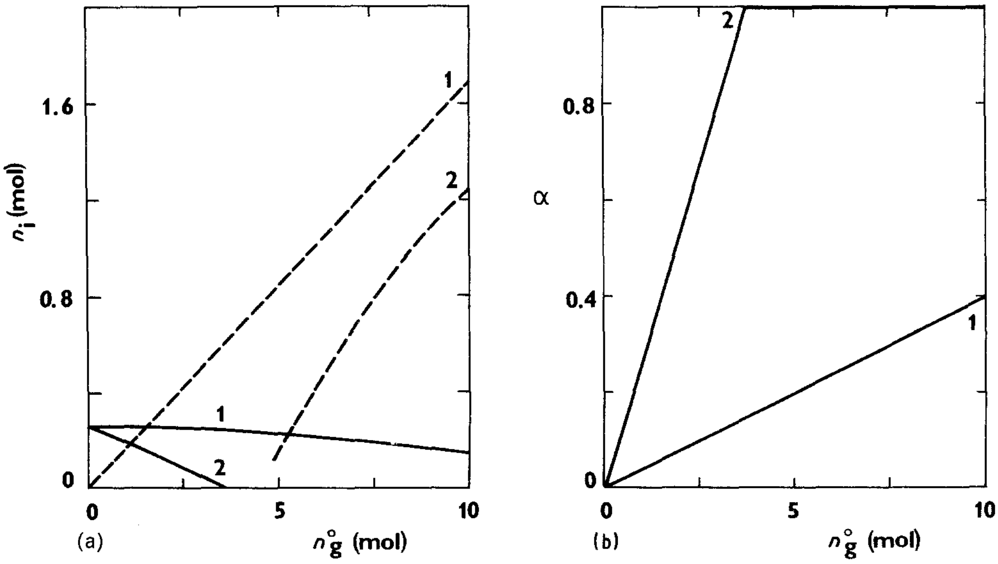

Figure 4 Dependences of the equilibrium amounts of boron (III) oxide and carbon (a) and of the degree of conversion of B_2O_3 initially present (b) on the total starting amount of gaseous phase. $x_{CCl_4}^0 = 0.20$; $T = 1200$ K; 1, $CCl_4 + H_2$; 2, $CCl_4 + NH_3$. (——) B_2O_3; (- - -) carbon.

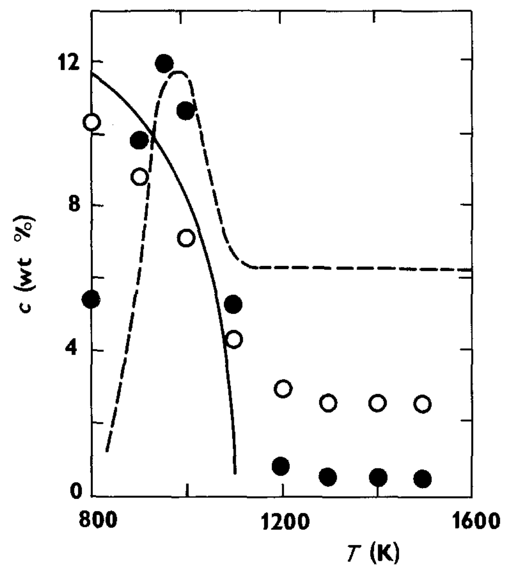

Figure 5 Comparison of calculated and observed composition, *c*, of the solid phase after technical boron nitride refining with $CHCl_3$ + NH_3 mixture. $x^0_{CHCl_3} = 0.205$; $n^0_g = 6.25$ mol. (——) oxygen calculated; (○) oxygen observed; (– – –) carbon calculated; (●) carbon observed.

with the $CCl_4 + H_2$ system it begins to form at very low n^0_g values, whereas with $CCl_4 + NH_3$, carbon only forms at $n^0_g > 3.75$ mol (for $n^0_g = 3.75$ mol, boron nitride is the only solid phase in equilibrium).

2.4. Comparison of calculated and observed solid phase composition after technical boron nitride refining

The calculated and observed temperature dependences of solid phase composition after refining with a $CHCl_3 + NH_3$ mixture are compared in Fig. 5. The calculated residual oxygen content agrees quite well with experimental data at temperatures up to approximately 1050 K; at higher temperatures, the calculations show that all initial boron (III) oxide reacts and oxygen is transferred to the gaseous phase, whereas experimentally, residual oxygen was detected in the refining product and its amount remained constant with increasing temperature of the process. This corroborates our hypothesis of the occurrence of boron–oxygen bonds of two kinds in the starting material, according to which, in addition to boron (III) oxide, oxygen is also bonded in the thermodynamically more stable boroxole ring [1]. This ring could not be included in the equilibrium calculations because of the lack of thermodynamic data.

The agreement between the calculated and observed carbon contents is very good up to a temperature of approximately 1100 K, the calculation also accounting for the observed sharp maximum. At temperatures in excess of 1100 K, the calculated as well as observed carbon content is virtually temperature-independent, the calculated value, however, is approximately 12 times higher. This can be explained so that in the experiment, chemical equilibrium had not established within the whole of the bulk of the gaseous phase, part of the $CHCl_3$ entering having remained unreacted, particularly at higher flow rates.

The results for the $CCl_4 + H_2$ system are compared in Table III. The calculated and observed carbon contents at 1000 K are in a good mutual agreement, at higher temperatures, however, the former is again about 12 times higher than the latter, which is explained as above. The residual oxygen data are in a good mutual agreement at 1300 K.

3. Conclusions

Some conclusions concerning suitable technological conditions for technical boron nitride refining by reductive chlorination can be drawn on the basis of the thermodynamic analysis of the B–N–O–C–Cl–H system.

1. The use of different methane chloro derivatives (CCl_4 or $CHCl_3$) gives rise to a different equilibrium composition of the system only at low temperatures, 800 to 900 K, the degree of conversion of the boron (III) oxide initially present being slightly higher and the amount of carbon formed slightly lower with $CHCl_3$, whereas at temperatures in excess of 1000 K the equilibrium composition for the two systems is virtually identical.

2. Substitution of hydrogen by ammonia has an appreciable positive effect: the degree of conversion of the initial B_2O_3 increases, the amount of carbon formed decreases and the overall boron balance improves, virtually all boron from the reacted boron (III) oxide being transformed into solid BN (this applies to initial concentrations of methane chloro derivative $x^0 < 0.30$).

3. The limiting factor in the reaction of boron (III) oxide is the supply of carbon to form carbon monoxide, the thermodynamically most stable oxygen-containing gaseous substance. The number of moles of the methane chloro derivative must, therefore, be at least three times higher than the number of moles of the B_2O_3 initially present. A high excess of methane chloro derivative over the 1 : 3 stoichiometric ratio does not raise the degree of conversion of boron (III) oxide appreciably; however, it increases the amount of carbon formed which contaminates the product and stimulates unwanted reactions of solid BN, giving rise to gaseous substances.

4. The temperature region 1100 to 1200 K is suitable for the refining process using ammonia-containing mixtures. At lower temperatures, oxygen is not removed from the technical boron nitride to a

TABLE III Comparison of calculated and observed solid phase composition after technical boron nitride refining with a $CCl_4 + H_2$ mixture, $x^0_{CCl_4} = 0.116$

Temperature (K)	Oxygen content (wt %)		Carbon content (wt %)	
	calculated	observed	calculated	observed
1000	10.13	6.72	14.70	12.10
1300	6.03	5.90	12.52	1.04

sufficient degree and, moreover, unwanted contamination of the product with carbon takes place. A higher temperature, on the other hand, does not usually result in an appreciable increase in the degree of conversion of the B_2O_3 initially present.

This thermodynamical analysis of the B–N–O–Cl–H system, which agrees well with experimental data [1], delineates the technological area of the process of refining turbostratic boron nitride, which contains residual boron (III) oxide as a product of imperfect nitridation. Reductive halogenation enables all oxide-bonded oxygen to be removed, and thereby powder with a preserved high sintering activity to be prepared at a relatively low cost.

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