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Optimal plasma process routes for boron nitride (BN) powder production from boric acid (H_3BO_3)

Života G. Kostić*, Predrag Lj. Stefanović, Pavle B. Pavlović, Dejan B. Cvetinović, Slobodan Đ. Šikmanović

The VINČA Institute of Nuclear Sciences, Laboratory for Thermal Engineering and Energy, PO Box 522, 11001 Belgrade, Yugoslavia

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Abstract

The results of equilibrium composition and total enthalpy computation in the temperature range of 1000 to 6000 K and at pressure of 1 bar, for the systems $\underline{B}\ \underline{O}\ \underline{H}\ \underline{N}$ and $\underline{B}\ \underline{O}\ \underline{C}\ \underline{H}\ \underline{N}$ are presented in the paper. These data enable the determination, and optimization of mass, temperature and energy parameters of the process for ultrafine boron nitride powder production by the boric acid (H_3BO_3) decomposition in nitrogen plasma, followed by reactive quenching with cold methane or propane–butane gas. In both cases for the optimized processes yield of boron nitride powder can be up to 100% in wide temperature range. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Computational plasma process; BN powder production

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1. Introduction

Boron nitride (BN) is a material with unique characteristics (excellent electrical insulator, excellent high temperature stability, high thermal conductivity, low dielectric constant, low loss tangent, low thermal expansion, excellent high temperature strength, chemically inert, easily machinable, low friction, non toxic, can be bonded to selected metals) which make it indispensable in wide variety of technical and industrial applications [1]. Thermodynamic consideration of $\underline{B}\ \underline{O}\ \underline{C}\ \underline{H}\ \underline{N}$ system for boron nitride powder production from boron trioxide (B_2O_3) as precursor was presented in the paper [1]. But the boron trioxide (B_2O_3) is very hygroscope (especially amorphous B_2O_3) and it is difficult to have dry solid B_2O_3 under ordinary conditions. For this reason it is more favorable to use the boric acid (H_3BO_3) as precursor.

This paper presents the results of thermodynamic considerations and optimization of $\underline{B}\ \underline{O}\ \underline{C}\ \underline{H}\ \underline{N}$ system, for boron nitride powder synthesis, by boric acid (H_3BO_3) decomposition in nitrogen plasma, followed by quenching with cold methane or propane–butane gas.

2. Computation method

Thermodynamic method used here [2], is based on the Mass Action Law. The first step in the thermodynamic modeling of the chemical equilibria involves a decision about the number of gas and condensed (solid or liquid) phase species to be considered. Let this number be m, the number of dense (solid and liquid) phase species be f and the number of atomic species be q, then $m - q$ mass action equations will determine equilibrium composition. In other words, $m-q$ equilibrium constants pertain. The equilibrium constants are usually specified for the decomposition reactions to the constituent atoms; all the equations being independent, such that

$$K_j(T) = \prod_{i=1}^{q} \frac{p_i^{a_{ij}}}{p_j} \quad (j = 1, 2, \ldots m - q) \tag{1}$$

where p_i are the partial pressures of the atomic species, p_j are the partial pressures of the molecular species, a_{ij} are the stoichiometric coefficients of decomposition reactions, and $K_j(T)$ are the mass action constants for decomposition into the atoms.

In the case of condensed (solid or liquid) substances that do not form solid solutions, the application of the mass action law, based on the constant saturation

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* Corresponding author. Tel.: +381-1145-5695; fax: +381-1145-3670.

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pressure (p_l^c) above the condensed phase at a fixed temperature (T), f other equations occur. These are of the form

$$K_l^c(T) = p_l^c \tag{2}$$

where subscript l indicates either atomic or molecular chemical species.

For an ideal gas mixture, Dalton's law is introduced in the form

$$\sum_{l=1}^{g} p_l = p \tag{3}$$

where g is the number of gas species and p is total pressure of the mixture.

In order to close the system of equation, the $q-1$ mass balance equations are included

$$\frac{\sum_{l=1}^{g} a_{ol} p_l + \sum_{cl=1}^{f} a_{ol} p \nu_l^c}{\sum_{l=1}^{g} a_{dl} p_l + \sum_{cl=1}^{f} a_{dl} p \nu_l^c} = \frac{O}{D} \tag{4}$$

where a_{ol} and a_{dl} are the numbers of o and d atomic species comprising product molecule l (the condensed phase of species l is denoted by cl), ν_l^c is the ratio of number of moles of condensed phase of constituent l to total number of moles in gas mixture, O and D are the o and d atomic species content in the reactants, respectively.

The total enthalpy of the system, H_s at temperature T, is calculated by adding an enthalpy of constituents (gaseous and condensed)

$$H_S(T) = n_g \left[\sum_{l=1}^{g} \nu_l H_l(T) + \sum_{l=1}^{f} \nu_l^c H_l^c(T) \right] \tag{5}$$

where n_g is the total number of moles in gaseous phase, ν_l is the mole fraction of gas constituent l, H_l (kJ/mol) and H_l^c (kJ/mol) are mole enthalpies of gas and condensed phase of constituent l respectively, defined by relationship

$$H_l(T) = -T^2 \left[\frac{\partial (G_l/T)}{\partial T} \right]_{p,\nu_l} = T^2 \left[\frac{\partial \Phi_l}{\partial T} \right]_{p,\nu_l} + \Delta_f H_l(T=0) \tag{6}$$

$\Delta_f H_l$ ($T = 0$) is the heat of formation of constituent l, from elements at standard state, for temperature $T = 0$ K, and Φ_l is the modified free enthalpy of constituent l defined as [3] (G, Gibss energy; S, entropy)

$$\Phi_l(T) = \frac{G_l(T) - H_l(T=0)}{T} = S_l(T) - \frac{H_l(T) - H_l(T=0)}{T} \tag{7}$$

For more details about computation method see Ref. [2].

The polynomial coefficients of the temperature dependence of a modified free enthalpies [2], chemical reaction enthalpy change, and the heat of formation (from elements at standard state and temperature $T = 0$ K) of constituents in the system, are taken from data [3] which are equivalent to those in JANAF [4] but more complete and more convenient for usage.

3. Results and discussions

The temperature dependence of the equilibrium composition for the $\underline{B}$ $\underline{O}$ $\underline{H}$ $\underline{N}$ system with atomic ratio B:O:H:N = 0.04:0.12:0.12:0.72 is given in Fig. 1. Only one condensed phase, boron oxide B_2O_3(s) can exist, for temperature $T < 2000$ K, in this system. All other species are in the gaseous state. A small mole fraction of B^+ ions and electrons exist at higher temperature only (about 0.1% for temperature $T = 6000$ K).

In Fig. 2, it is shown the temperature dependence of the equilibrium composition for the $\underline{B}$ $\underline{O}$ $\underline{C}$ $\underline{H}$ $\underline{N}$ system with atomic ratio B:O:C:H:N = 0.025:0.075:0.075:0.375:0.45, which can be obtained by injection of

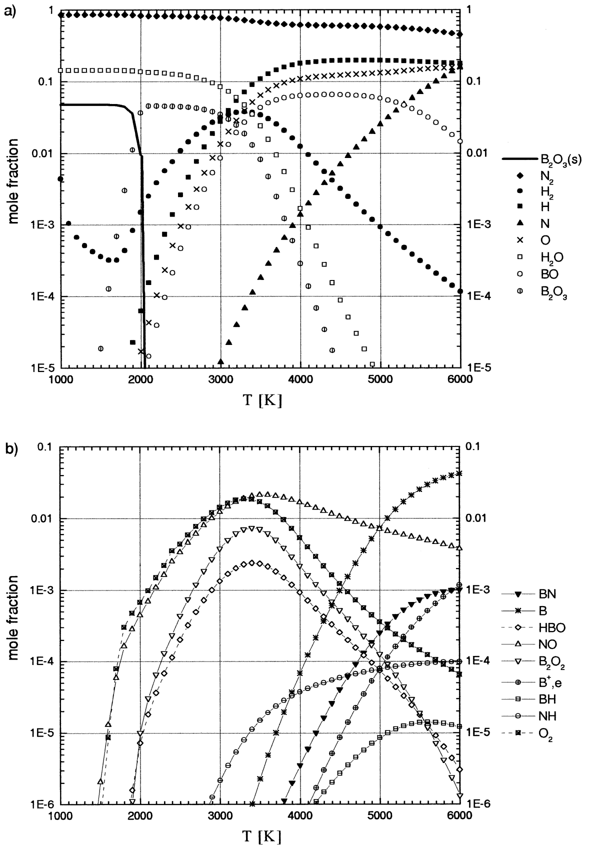

Fig. 1. Equilibrium composition of the B_O_H_N system for B:O:H:N = 0.04:0.12:0.12:0.72: (a) main constituents, (b) other species.

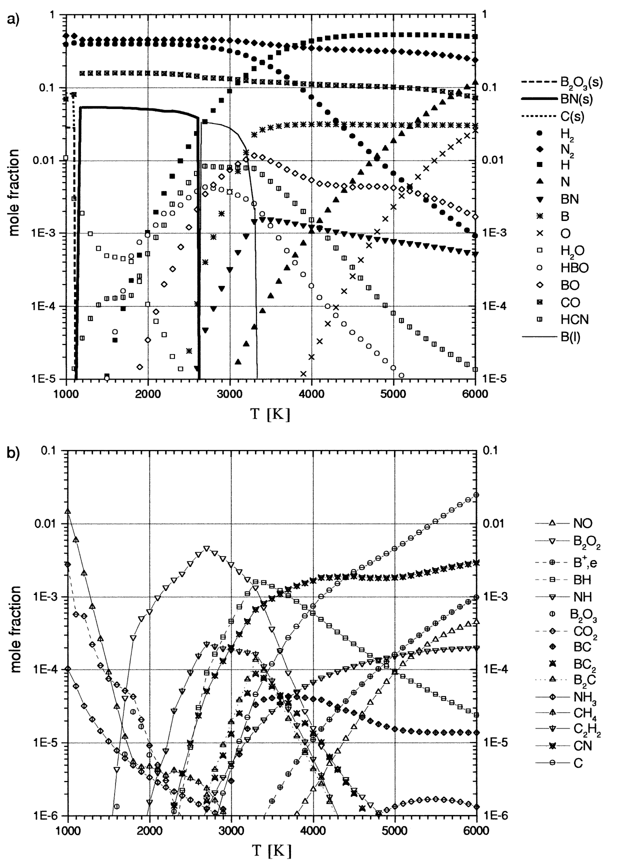

Fig. 2. Equilibrium composition of the system for B:O:C:H:N = 0.025: 0.075:0.075:0.375:0.45: (a) main constituents, (b) other species.

adequate quantity of methane in the system from Fig. 1. Four condensed phases, B_2O_3(s), C(s), BN(s), and B(l), can exist in this system. The pure boron nitride powder, BN(s) can be deposited in the wide temperature interval 1200 K < T < 2600 K (Fig. 2). In the temperature range from 2600 to 3300 K (Fig. 2) B-droplets, B(l), can be condensed, and this region must be passed quickly if we want to synthesize pure boron nitride powder. All other species are in the gaseous state. A small mole fraction of B^+ ions and electrons exist at higher temperature only (less then 0.1% for temperature T = 6000 K).

The presented results indicates technological steps in plasma chemical process for boron nitride powder synthesis from boric acid (H_3BO_3) as precursor. In the first step, boric acid powder injected in nitrogen plasma is evaporated and decomposed: as a result of this process the nitrogen plasma partially cools, and gives adequate B O H N system. In the second step, a sufficient quantity of methane is injected, as reduction and cooling reagent, in the B O H N system. This process gives adequate B O C H N system and, in the corresponding temperature range (1200 K < T < 2600 K), boron nitride powder.

The temperature dependence of total enthalpy (per one mol*) for B–O–H–N system is presented in Fig. 3. One mol* is defined as the quantity of the system, which consist of one mole of atoms (of all elements in the systems) in total. For example, 1 mol* of the system in Fig. 1 consist 0.04 mole of B atoms plus 0.12 mole of O atoms plus 0.12 mole of H atoms plus 0.72 mole of N atoms. The enthalpy of nitrogen plasma is also shown.

3.1. Optimal process for reactive quenching with cold methane gas

The system from Fig. 1, can be obtained from 0.04 mole of boric acid (H_3BO_3) injected to 0.72 mol* of nitrogen plasma. The inlet enthalpy of crystalline boric acid (H_3BO_3) at temperature T = 298.15 K is $H_{\mathrm{H3BO3,in}} = -1067.96$ kJ/mol (calculated from data [3]). If the temperature of nitrogen plasma is $T_1 = 5700$ K, from Fig. 3 (curve 1) we can find that the enthalpy of nitrogen plasma is $H_{\mathrm{s},1} = 136$ kJ/mol*. With the assumption that there are no heat losses to surroundings, the enthalpy of the B:O:H:N = 0.4:0.12:0.12:0.72 will be

$$H_{\mathrm{s},2} = 0.04 \times H_{\mathrm{H3BO3,in}} + 0.72 \times H_{\mathrm{s},1}$$
$$= 0.04 \times (-1067.96) + 0.72 \times 136 = 55.2\,\mathrm{kJ/mol}^*$$

For this enthalpy value in Fig. 3 (curve 9) one can find that the corresponding temperature of the system is $T_2 \approx 3300$ K.

If we inject 0.075 mole of cold methane, whose enthalpy at T = 298.15 K is [3] $H_{\mathrm{CH4,in}} = -56.614$ kJ/mol, to 5/8 of mol* of the system B:O:H:N = 0.04: 0.12:0.12:0.72 (Fig. 1) for which has been calculated enthalpy $H_{\mathrm{s},2} = 55.2$ kJ/mol*, the atomic content of

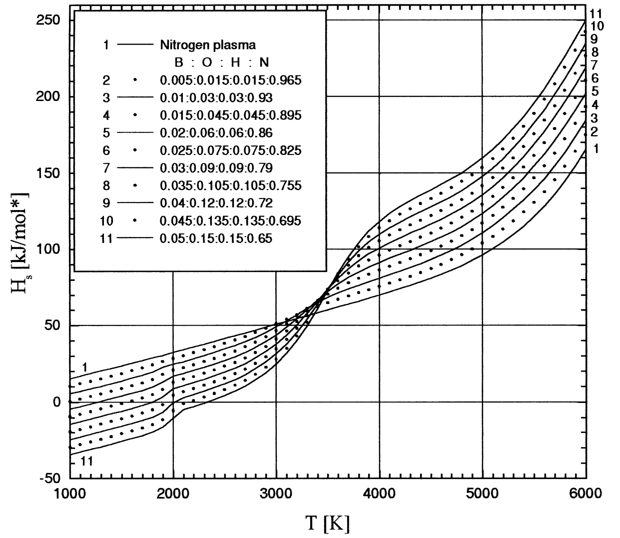

Fig. 3. Temperature dependence of enthalpy for the B–O–H–N systems, at p = 1 bar.

newly obtained system is B:O:C:H:N = 0.025:0.075:0.075:0.375:0.45. The enthalpy of this system will be

$$\begin{aligned} H_{s,3} &= (5/8) \times H_{s,2} + 0.075 \times H_{CH4,in} \\ &= (5/8) \times 55.2 + 0.075 \times (-56.614) \\ &= 30.25\,\mathrm{kJ/mol^*}. \end{aligned}$$

In Fig. 4 for B:O:C:H:N = 0.025:0.075:0.075:0.375:0.45 (curve 8) and for enthalpy value of 30.25 kJ/mol*, we can find that corresponding temperature of the system is $T_3 \approx 2500$ K.

Optimization is an iterative (variation) calculation procedure, based on data as those presented in Figs. 3 and 4. It is obvious that only the last iteration is presented in previous calculation, in which the heat losses to the surroundings were neglected. For more realistic case and presumption that heat losses to surroundings are $q_1 = 20$ kJ/mol* (first step of the process) and $q_2 = 10$ kJ/mol* (second step of the process) we will obtain following results for system enthalpies and temperature

$$\begin{aligned} H_{s,2} &= 0.04 \times H_{5H3BO3,in} + 0.72 \times H_{s,1} - q_1 \\ &= 0.04 \times (-1067.96) + 0.72 \times 136 - 20 \\ &= 35.2\,\mathrm{kJ/mol^*} \end{aligned}$$

For this enthalpy value in Fig. 3 (curve 9) one can find that the corresponding temperature of the system (with the atomic content of B:O:H:N = 0.4:0.12:0.12:0.72) is $T_2 \approx 3100$K.

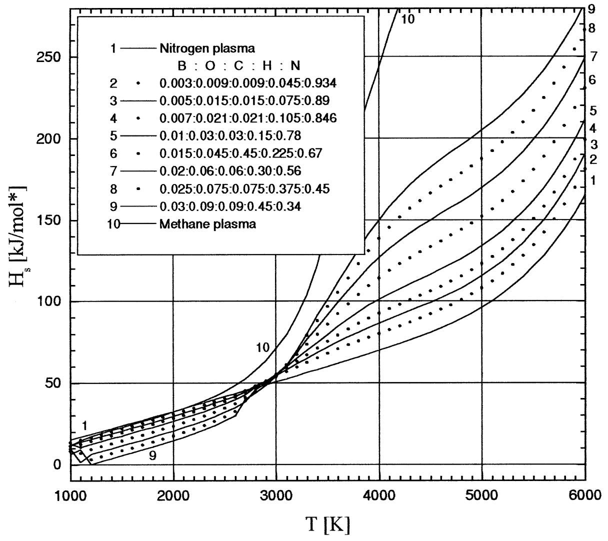

Fig. 4. Temperature dependence of enthalpy of B–O–C–H–N systems (at $p = 1$ bar) which are obtained by mixing of adequate quantity of H_3BO_3 and CH_4 with nitrogen plasma.

$$\begin{aligned} H_{s,3} &= (5/8) \times H_{s,2} + 0.075 \times H_{CH4,in} - q_2 \\ &= (55/88) \times 35.2 + 0.075 \times (-56.614) - 10 \\ &= 7.75\,\mathrm{kJ/mol^*} \end{aligned}$$

For this enthalpy value in Fig. 4 (curve 8) one can find that the corresponding temperature of the system (with the atomic content of B:O:C:H:N = 0.025:0.075:0.075:0.375:0.45) is $T_3 \approx 1500$ K.

3.2. Optimal process for reactive quenching with cold propane–butane gas

Iterative procedure similar to that in Section 3.1, gives following results for optimal process in case when reactive quenching is conducted with cold propane–butane gas. In the first step of the process by injection of 0.034 mole of boric acid (H_3BO_3) to 0.762 mol* of nitrogen, the system $\underline{\mathrm{B}}$ $\underline{\mathrm{O}}$ $\underline{\mathrm{H}}$ $\underline{\mathrm{N}}$ = 0.034:0.102:0.102:0.762 is obtained. With the assumption that there are no heat losses to surroundings, the enthalpy of the system B:O:H:N = 0.034:0.102:0.102:0.762 will be

$$\begin{aligned} H_{s,2} &= 0.034 \times H_{H3BO3,in} + 0.762 \times H_{s,1} \\ &= 0.034 \times (-1067.96) + 0.762 \times 136 \\ &= 67.32\,\mathrm{kJ/mol^*}. \end{aligned}$$

For this enthalpy value in Fig. 3 (near to curve 8) one can find that the corresponding temperature of the system is $T_2 \approx 3400$ K.

Enthalpy of propane–butane gas (40% propane 60% butane mixture, with conditional molecular formula $C_{3.6}H_{9.2}$) at $T = 298.15$, $H_{C3.6H9.2,in} = -100.95$ kJ/mol, has been calculated from enthalpy values of butane and propane [5] and theirs heat of formation [6]. In the second step of the process 0.02083 mole of $C_{3.6}H_{9.2}$ (propane–butane) is injected to 0.735 mol* of the system B:O:H:N = 0.034:0.102:0.102:0.762. The atomic content of newly obtained system is B:O:C:H:N = 0.025:0.075:0.075:0.266:0.560. The enthalpy of this system will be:

$$\begin{aligned} H_{s,3} &= 0.375 \times H_{s,2} + 0.02083 \times H_{C3.6H9.2,in} \\ &= 0.735 \times 67.32 + 0.02083 \times (-100.95) \\ &= 47.38\,\mathrm{kJ/mol^*} \end{aligned}$$

In Fig. 5 for B:O:C:H:N = 0.025:0.075:0.075:0.267:0.558 (curve 6) and for enthalpy value of 47.38 kJ/mol*, we can find that corresponding temperature of the system is $T_3 \sim 2900$ K.

For the presumption that heat losses to surroundings are $q_1 = 25$ kJ/mol* (first step of the process) and $q_2 = 10$ kJ/mol* (second step of the process) we will obtain

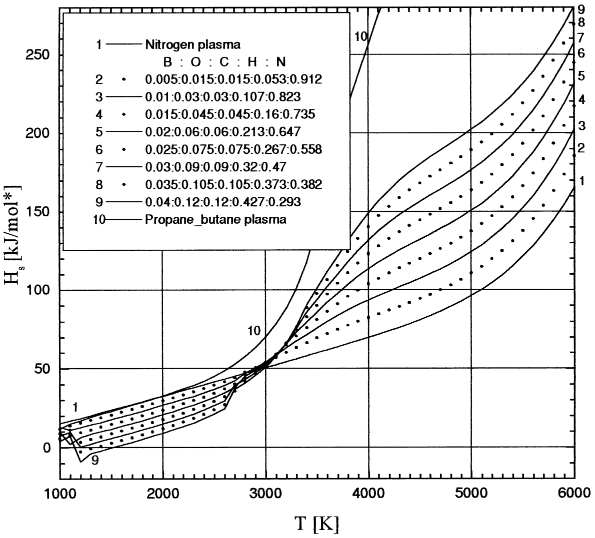

Fig. 5. Temperature dependence of enthalpy of B–O–C–H–N systems (at $p = 1$ bar) which are obtained by mixing of adequate quantity of H_3BO_3 and $C_{3.6}H_{9.2}$ with nitrogen plasma.

following results for the enthalpies and temperature of the system

$$H_{s,2} = 0.034 \times H_{H3BO3,in} + 0.72 \times H_{s,1} - q_1$$
$$= 0.034 \times (-1067.96) + 0.762 \times 136 - 25$$
$$= 42.32\,\mathrm{kJ/mol^*}$$

$$T_2 \sim 2800\,\mathrm{K}$$

$$H_{s,3} = 0.735 \times H_{s,2} + 0.02083 \times H_{C3.6H9.2,in} - q_2$$
$$= 0.735 \times 42.32 + 0.02083 \times (-100.95) - 10$$
$$= 19.0\,\mathrm{kJ/mol^*}$$

$$T_3 \sim 2000\,\mathrm{K}$$

The temperature dependence of the equilibrium composition for the $\underline{B}$ $\underline{O}$ $\underline{C}$ $\underline{H}$ $\underline{N}$ system with atomic ratio B:O:C:H:N = 0.025:0.075:0.075:0.267:0.558 is given in Fig. 6. The pure boron nitride powder, BN(s) can be deposited in the wide temperature interval 1200 K < T < 2700 K (Fig. 6). In the temperature range from 2700 to 3300 K (Fig. 6) B-droplets, B(l), can be condensed, and this region must be passed quickly if we want to synthesize pure boron nitride powder. All other species are in the gaseous state. A small mole fraction of B+ ions and electrons exist at higher temperature only (about 0.1% for temperature $T = 6000$ K).

The yield of boron nitride powder [number of moles of BN(s) per mole of B atoms in the system] (Figs. 7 and 8) in temperature range 1200 K < T < 2000 K is close to 1 (theoretical maximum).

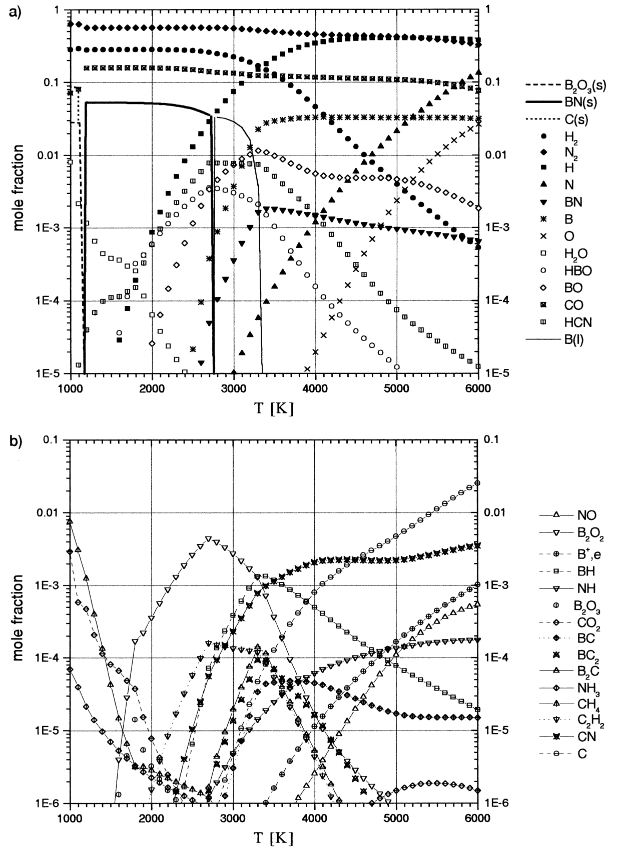

Fig. 6. Equilibrium composition of the system for B:O:C:H:N = 0.025:0.075:0.075:0.267:0.558: (a) main constituents, (b) other species.

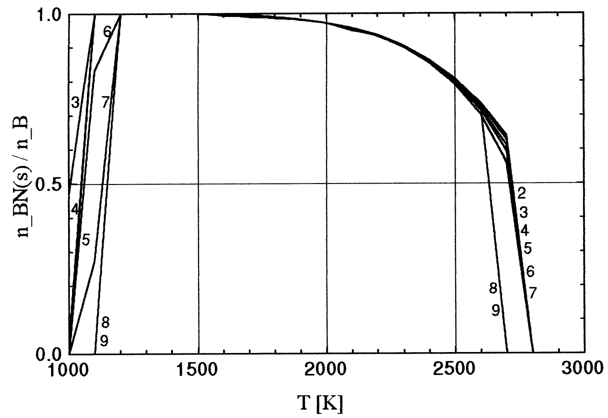

Fig. 7. The yield of boron nitride powder $\underline{n}$ $\underline{B}$N(s)/$\underline{n}$ $\underline{B}$ for quenching with methane (legend is the same as in Fig. 4).

From equilibrium consideration it is not possible to make any conclusion about boron, B(l), nucleation and condensation in temperature range 2700 K < T < 3300 K (Fig. 2) and 2800 K < T < 3300 K (Fig. 6). For homogeneous nucleation, which will occur in the system without the foreign particles, the Kelvin effect [2,7] sets

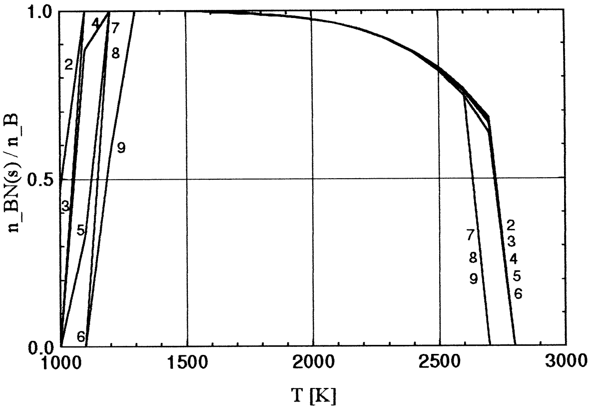

Fig. 8. The yield of boron nitride powder n_BN(s)/n_B for quenching with propane–butane (legend is the same as in Fig. 5).

Table 1
Saturation ratio $S_B = p_B/p_{B,sat}$

$T(K)\rightarrow$	2700	2800	2900	3000	3100	3200	3300	Notes
S_B (1)	5.64	5.50	4.49	3.39	2.40	1.62	1.06	For the system in Fig. 2
S_B (2)		5.97	4.82	3.62	2.52	1.69	1.11	For the system in Fig. 6

a lower limit on the droplet size that can serve as condensation nuclei. In the absence of the other experimental data, it is usual to take the value of supersaturation about 10, for rough estimation of stable nucleus formation. As can see from Table 1, homogenous nucleation and condensation of boron can not occur between 2700 and 3300 K, due to the fact that $S_B \leqslant 5.97$ in whole this temperature range. Value of $S_B = p_B/p_{B,sat}$ (p_B, partial pressure of B) has been calculated with assumption that in the system there is no condensation of boron for $T > 2700$ K.

4. Conclusion

The presented results of thermodynamic computation (of the equilibrium composition and total enthalpy behavior) of the B–O–H–N and B–O–C–H–N systems enables the determination and optimization of the temperature, mass and enthalpy parameters for production of boron nitride powder in nitrogen plasma from boric acid (H_3BO_3) powder as a precursor. The method of process parameter determination and optimization is illustrated by two examples: for reactive quenching with cold methane or with cold propane-butane gas, in the second step of the process.

In the first step of the process, boric acid powder injected in nitrogen plasma is evaporated and decomposed: as a result of this process the nitrogen plasma partially cools, and gives adequate B–O–H–N system. In the second step of the process in the B–O–H–N system is injected a sufficient quantity of methane or propane-butane, as reduction and cooling reagents; this process gives adequate B–O–C–H–N system and, in the corresponding temperature range, boron nitride powder.

The results of such calculations enable to cut down experimental work and decrease the cost of investigations.

References

[1] Ž.G. Kostić, P.Lj. Stefanović, P.B. Pavlović, Thermodynamic consideration of B–O–C–H–N system for boron nitride powder production in thermal plasma, in: C. Galassi (Ed.) Fourth Euro Ceramics—Basic Science—Developments in Processing of Advanced Ceramics—Part I, Vol. 1, 1995, pp. 307–314.

[2] Ž.G. Kostić, P.Lj. Stefanović, P.B. Pavlović, Ceramics International 22 (1996) 179–186.

[3] V.P Glushko, L.V. Gurevich (Eds.), Termodinamicheskie svoistva individualnyikh veshchestv, Nauka, Moskva, (T.I) 1978, (T.II) 1979, (T. III) 1981.

[4] D.R. Stull, H. Prophet, (Pr. Dir.) JANAF Thermochemical Tables, 2nd ed., NSRDS-NBS 37, USA, June 1971.

[5] N.B. Vargaftik, Spravochnik po teplofizicheskim svoistvam gazov i zhidkostei, Gos. Izd. fiz. mat. lit., Moskva, 1963, pp. 173, 192.

[6] L.W. Nelson, Petroleum Refinery Engineering, McGraw–Hill, New York/London, 1969, p. 709.

[7] S.K. Friedlander, Smoke, Dust and Haze, Fundamentals of Aerosol Behavior, John Wiley & Sons, New York, London, 1977, p. 235.