Determining Gas Composition for Growth of BNNTs Using Thermodynamic Approach

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Abstract

A high-yield production of high-quality boron-nitride nanotubes (BNNTs) was reported recently in several publications. A boron-rich material is evaporated by a laser or plasma in a nitrogen-rich atmosphere to supply precursor gaseous species for nucleation and growth of BNNTs. Either hydrogen was added or pressure was increased in the system to achieve high yield and high purity of the synthesized nanotubes. According to the widely-accepted “root grow” mechanism, upon the gas cooling, boron droplets form first, then they adsorb nitrogen from surrounding gas species, and BNNTs grow on their surfaces. However, what are these precursor species that provide nitrogen for the growth is still an open question. To answer this question, we performed thermodynamic calculations of B-N mixture composition considering broad set of gas species. In enhancement of previous studies, the condensation of boron is now taken into account and is shown to have drastic effect on the gas chemical composition. B$_2$N molecules were identified to be a major source of nitrogen for growth of BNNTs. Presence of B$_2$N molecules in a B-N gas mixture was verified by our spectroscopic measurements during a laser ablation of boron-rich targets in nitrogen. It was shown that the increase of pressure has a quantitative effect on the mixture composition yielding increase of the precursor density. The effect of hydrogen addition was studied as well. In addition, thermodynamics was applied in conjunction with agglomeration theory to predict the size of boron droplets upon growth of BNNTs. Analytical relations for identification of crucial species densities were derived.

I. Introduction

Boron-nitride nanotubes (BNNTs) attract significant interest because of their unique properties not available in other nanomaterials, such as high Young’s modulus, excellent thermal conductivity,
superhydrophobicity\textsuperscript{4}, relatively lower rigidity in the transverse direction\textsuperscript{5} and chemical stability up to 900°C in air. The nanotubes are wide band gap semiconductors with a very small dependence on the chirality\textsuperscript{6}. Carbon doping of BNNTs offers a possibility of tailored electrical properties of a nanotube\textsuperscript{7,8}. BNNTs can be applied for electroporation-based oncology therapies\textsuperscript{9}. There is an increasing amount of works devoted to synthesis of BNNTs. A thorough review on BNNTs production methods, properties and applications can be found in Ref. [10].

Successful high-selectivity production of high-quality BNNTs was reported in atmospheric and higher pressure systems, including the arc ablation\textsuperscript{11,12} and laser ablation\textsuperscript{13,14,15} reactors and, more recently, in inductively-coupled plasma (ICP) systems\textsuperscript{16,17,18}. The later offers scalable high-yield production of BNNTs at relatively low cost. Noteworthy that these methods enabled production of BNNTs without addition of any metallic catalysts to the synthesis process. In both these methods, solid boron or boron-rich material in a bulk or powder form is evaporated in nitrogen atmosphere by a laser or high-temperature ICP plasma forming B-N atomic gas mixture at high gas temperatures. In colder regions, the gas condenses resulting in formation of nanoparticles.

A commonly accepted mechanism of the formation of BNNTs from the condensing gas is so-called “root-growth” mechanism, first proposed in Ref. [13] based on results of ex-situ analysis, then supported in Refs. [16] and [17], and later witnessed by ab-initio molecular dynamic simulations and arc synthesis experiments\textsuperscript{19}. According to the root-growth concept, when B-N gas mixture cools down, boron gas condenses first and droplets of liquid boron form. Then, boron within the droplets reacts with nitrogen-containing radicals from the ambient gas, and BNNTs grow out from the droplets surfaces. However, what are these gas species that provide nitrogen for the BNNTs growth is still an open question. In Ref. [16], for instance, it is assumed that N\textsubscript{2} molecules might be precursors for the growth of BNNTs. However, it is questionable whether N\textsubscript{2} molecules can serve as precursors for the formation of periodic (hexagonal) B-N solid structures because this transformation is energetically unfavorable: N\textsubscript{2} molecules have high binding energy of 9.8 eV whereas B-N bond energy is about 4.0 eV. Other gaseous species such as atomic nitrogen N and BN, BN\textsubscript{2} and B\textsubscript{2}N molecules look more favorable precursors for formation of hexagonal BN structures.

In recent molecular dynamics simulations\textsuperscript{20}, several atomic and molecular gas species were tried as “building blocks” to produce solid BN structures. It was shown that tube-like and cage-like BN structures can be efficiently formed from BN molecules. However, these simulations have been performed with pre-defined gas composition; in particular, pure BN molecules gas and pure borazine gas were separately considered. In practice, the feedstock material is introduced into plasma, evaporates and is subsequently transported to the reaction zone\textsuperscript{16,17,21}. In this zone, under definite temperature conditions, boron starts to condense and nanotubes form. In this process, composition of the gas mixture cannot be arbitrary prepared; it is determined by chemical reactions between the gas species. What can be controlled is feedstock material, pressure and temperature within the system and buffer gas composition\textsuperscript{22,23}. Molecular dynamics simulations are not capable of modeling long time-
scale processes of material evaporation, cooling and condensation; different method should be applied to determine actual gas mixture composition at the nanoparticles growth.

Interestingly, for all plasma-based BNNT production methods (laser ablation, arc discharge and ICP plasma) rather low production rates were observed at atmospheric pressure: many of the boron droplets ended up with no nanotubes grown on them. Increase of the pressure up to 10 atm. in Ref. [16] and up to 20 atm. in Ref. [14] resulted in substantially higher production yield of the nanotubes and their purity measured in terms of quantity of the nanotubes to the rest of synthesized product. There were also studies where even higher pressures were tried, up to 68 atm. Another approach to increase the yield of BNNTs was found in Refs. [17] and [18]: it was shown that addition of hydrogen to the working gas can increase the yield and purity of the nanotubes produced even without increase of pressure. It is interesting to investigate the gas mixture compositions in these systems and to identify which gas species are crucial precursors for efficient growth of BNNTs.

Thermodynamic modeling is well suitable for finding composition of a chemically reacting system close to equilibrium state. There are several studies devoted to determining composition of the B-N gas mixture at various temperatures. In Ref. [29], a broad set of gas species was considered including three-atomic molecules B$_3$, B$_2$N and BN$_2$. Intriguingly, B$_2$N molecules were shown to be dominant species at lower temperatures corresponding to formation of solid BN structures suggesting them as a main precursor for growth of BNNTs. However, in previous thermodynamic computations, condensation of boron was not taken into account (only gas phase species were considered) resulting in overestimation of boron-containing gas species densities at low temperatures where BNNTs grow.

In this paper, we present the results of thermodynamic calculations for B-N system equilibrium composition at atmospheric and increased pressures with and without addition of hydrogen. A broad set of B, N and H containing gas species from [29] was considered with thermodynamic data from Refs. [31] and [32]. Liquid boron and solid BN were taken into consideration as well. This allowed us to account for condensation of boron and determining the conditions for solid BN formation.

Similar thermodynamic approach was previously used in Refs. [33], [34] and [35] to calculate carbon-helium gas mixture composition with condensation of carbon. In Ref. [34], species density profiles in a carbon arc for synthesis of nanoparticles were computed and compared to in-situ measurements. A good agreement with experimental data on species density profile was obtained in Ref. [34], despite fast flow, sharp density gradients and oscillations of the arc showing that chemistry is much faster than other processes and equilibrium assumption can be applied when determining mixture composition for synthesis applications. Computations results for the B-N system were verified by comparison to optical emission spectroscopy (OES) data from our experiments on laser ablation of boron-rich targets in nitrogen atmosphere and to OES measurements [18] in the ICP plasma reactor.
The paper is organized as follows. In section II, thermodynamic method based on minimization of Gibbs free energy for determining equilibrium composition of chemically reacting mixture containing gas, liquid and solid species is described. Section III is devoted to results of the thermodynamic calculations and their analysis. In subsection III.A, effect of gas condensation on the gas mixture composition is evaluated. In subsections III.B and III.C, effects of pressure variation and hydrogen addition on mixture composition and densities potential precursors for growth of BNNTs are studied. Subsection III.D is devoted to verification of the thermodynamics results via comparison to spectroscopic data for ICP reactor [18]. Subsection III.E describes experimental setup used for laser ablation of boron-rich targets and presents OES measurements results. In subsection III.F, the thermodynamics results are used in conjunction of with a simple agglomeration theory to predict size of boron droplets by the time when BNNTs start growing on them and they are solidified. In subsection III.G, analytic relations for densities of major mixture components are derived. Finally, the conclusions are formulated.

II. Method for determining equilibrium chemical composition

For mixtures containing few components, a composition can be conveniently determined using thermodynamic equilibrium constants for decomposition and ionization reactions, together with the mass conservation law and electrical neutrality, see Ref. [36] and references therein. For more complex mixtures, as we have here, number of chemical reactions between different species becomes very large, and a different approach, based on the minimization of the Gibbs free energy, is more suitable.

According to the second law of thermodynamics, when a thermodynamic system reaches equilibrium state at given temperature and pressure its Gibbs free energy is at its minimum. Constant pressure is a good approximation when considering any gas volume moving with the flow because Mach numbers in the reactors are normally very low (much less than unity). Typically, temperature variation characteristic time is larger than time required for chemical composition to change, hence, mixture composition can be considered in chemical equilibrium and thermodynamic approach can be applied. Simple description of the Gibbs free energy minimization method for gas mixtures can be found in Refs. [26] and [27].

The Gibbs free energy of a multi-component system (or mixture) can be expressed as a sum of chemical potentials of its individual component species \( \mu_i \) multiplied by their quantities \( N_i \) (numbers of atoms or molecules) within the closed system (arbitrary chosen volume moving with the fluid flow) under consideration as \(^{37,38}\):

\[
G = \sum_i N_i \mu_i .
\]

For the gas species, chemical potential can be expressed (in ideal gas approximation) as \(^{27,37,38,39}\):

\[
\mu_i = R T \ln(p_i / p_{i0}^{eq}) + RT \ln \left( \frac{N_i}{N_i^{eq}} \right) + RT \ln(1 + \alpha_i)
\]
\[ \mu_i = RT \ln \frac{P_i}{p_0} + G_i^f (p_0, T) = RT \left( \ln x_i^* + \ln \frac{P}{p_0} \right) + G_i^f (p_0, T). \]  

(2)

Here, \( G_i^f (p_0, T) \) is the molar Gibbs energy of the component \( i \) in its pure state, at standard pressure \( p_0 = 1 \text{ atm} \) and given temperature \( T \), or, in other words, it is the Gibbs energy of formation of species \( i \) from its constituting elements in their standard states at temperature \( T \) (the Gibbs energy of formation of any species in its standard state is commonly considered zero); \( p_i \) is its partial pressure; \( p \) is pressure in the system \( x_i \) is molar fraction of species \( i \) among other gaseous species (excluding solid and liquid species):

\[ x_i = \frac{N_i}{\sum_{k=\text{gas species}} N_k}. \]  

(3)

For incompressible solid and liquid species, the energy does not depend on pressure, and the expression for chemical potential reduces to:

\[ \mu_i = G_i^f (T). \]  

(4)

Equilibrium composition of a mixture of known gaseous, liquid and solid components can be determined as a set of \( N_i \) which gives the minimum value of the Gibbs energy (1) and satisfies constraints of conservation chemical elements of each sort of atoms within the system:

\[ \sum_i a_{i,j} N_i = b_j N^* ; j = 1, 2, ..., m. \]  

(5)

Here, \( m \) is the number of different sorts of atoms (different chemical elements) within the system, \( b_j \) is mole fraction of element \( j \) within the system, \( a_{i,j} \) is number of atoms of sort \( j \) in species \( i \), and \( N^* = \sum_{i=\text{all spec.}} \left( N_i \sum_j a_{i,j} \right) \) is the total number of various atoms in all species within the system. Because densities and molar fractions of species usually are of interest (not absolute numbers of atoms and molecules), \( N^* \) can be chosen arbitrary.

Charge conservation needs to be maintained as well:

\[ \sum_i Z_i N_i = 0. \]  

(6)

Here \( Z_i \) is the charge number of species \( i \); \( Z_i = -1 \) for electrons.
Substitution of \( \mu_i \) defined by (2) and (4) into (1), using (3), yields following function of species quantities \( N_i \) to be minimized:

\[
RT \sum_{i, \text{gas}} N_i \left( \ln N_i - \ln \left( \sum_{k, \text{gas}} N_k \right) + \ln \frac{P_i}{P_0} \right) + \sum_{i, \text{all}} N_i G_i^f (p_0, T) \rightarrow \min.
\]

(7)

Here, \( N_i \) are absolute quantities of species within the system. Densities and partial pressures of gaseous species \( n_i \) can be derived from their molar fractions, \( x_i^* \), defined in (3):

\[
p_i = x_i p; \quad n_i = x_i \frac{p}{kT}.
\]

(8)

Simultaneous consideration of solid and liquid species allows accurate accounting for condensation/solidification happening in the considered gas volume at constant pressure and slowly changing temperature.

For B-N and B-N-H mixtures we consider broad set of species including various triatomic molecular gases considered in Ref. [29]. Gibbs energies of formation \( G_i^f (p_0, T) \) for gases N, N\(_2\), N\(_3\), B, B\(^+\), B\(_2\), H, H\(_2\), NH, NH\(_2\), N\(_2\)H\(_2\), N\(_2\)H\(_4\), NH\(_3\), BH, BH\(_2\), BH\(_3\), and \( G_i^f (T) \) for liquid/solid B and solid (crystalline) BN were taken from NIST-JANAF reference\(^{31}\) where they are tabulated as functions of temperature at atmospheric pressure. For the sake of simplicity, only atomic boron ions were considered; ions of other species have very low densities in these equilibrium calculations with the temperature range of interest (below 6 000 K)\(^{28, 29}\).

Unfortunately, for other gas species observed in plasma and laser ablation of boron-rich targets in inert gas atmosphere, such as B\(_2\)N\(_4\), B\(_3\), and BN\(_2\) molecules, thermodynamic data is not given in tables [31]. Nevertheless, for these molecules, free energy of their association from constituting atoms (in some other sources also referred as dissociation energy) was computed \textit{ab-initio} in Ref. [32] using quantum chemistry package Gaussian-86\(^{44}\). These data allows easy obtaining Gibbs energy of formation for these molecules which can be self-consistently used use with other Gibbs free energy data on species from Ref. [31]:

\[
G_i^f (p_0, T) = \sum_j a_{i,j} G_j^f (p_0, T) - \Delta G_i^f (T).
\]

(9)

Here, \( G_i^f (p_0, T) \) is the Gibbs energy of formation of a molecule \( i \), \( \Delta G_i^f (T) \) is its free energy of association\(^{32}\), the summation in the right-hand side is performed over various atoms within the molecule, \( G_j^f (p_0, T) \) is Gibbs energy of the atoms in gaseous state\(^{31}\), and again \( a_{i,j} \) is number of atoms of sort \( j \) in a molecule \( i \). Note that in Ref. [32], for molecules having several isomers, e.g. B\(_2\)N,
individual contributions of various isomers are weighted and the global thermodynamic quantity was presented making implementation of the data very convenient.

In principle, even larger molecules constituting of B and N atoms, such as B$_2$N$_2$, BN$_3$ and B$_3$N were observed in some of the experiments$^{41,42}$. However, lack of thermodynamic data for these molecules did not allow taking them into consideration. In this regard B$_2$N can be viewed as a proxy for other larger molecules, similar to what was observed for carbon where many molecular species can be accounted for$^{33,45}$.

Additional complication is that the thermodynamic data for BN molecules$^{31}$ is given with a very high level of uncertainty. Free energy of formation is calculated based on dissociation energy for which uncertainty is about 70%: its value varies between 4 eV and 7 eV for the standard conditions, depending on literature. Such ambiguity in the energy of formation would result in substantial uncertainty (of several orders of magnitude) in computed BN molecules density in the equilibrium B-N mixture. Noteworthy that in Ref. [31] rather old literature was considered when constructing the table for BN molecules, 1964 and before. Newer sources [32, 46, 47, 48, 49, 50] are more consistent on the value of BN dissociation energy at standard conditions, giving values varying from 3.9 eV to 4.5 eV. Possible explanation for such variety of the dissociation energy values in old papers can be deducted from Ref. [49] where it is explained that binding (or dissociation) energy of BN molecule depends on whether it is considered to be in a ground state 3Π or excited state 1Σ. For the ground state, adequate for our temperatures of interest, binding energy is about 4 eV. For our thermodynamic modeling, we calculated free energy of association $\Delta G_f^i (T)$ for BN molecules using thermodynamic data from Ref. [32], to be consistent with data for other molecules. We also tried thermodynamic data for BN from newer source [48], there were some quantitative changes in the BN densities but the picture did not change qualitatively. The energy was calculated from equilibrium constant $K_f$ for the formation reaction: $\Delta G_f^i (T) = -RT \ln K_f$.

III. Results and discussion

III.A. Effect of boron condensation on the species densities

Computed composition of B-N mixture (with no hydrogen), is shown in Figures 1 and 2 as a function of temperature. Figure 1 displays effect of boron condensation on species densities. Two computational runs were performed. In one run, single phase calculation was performed – only gas phase species were considered. Their densities are presented partially as solid lines for T>4137 K (4137 K is the boiling point of liquid boron at atmospheric pressure) and dashed lines, for T<4137 K. Different colors represent different species. In another run, liquid boron and solid BN were added to the system allowing accounting for boron condensation and solid BN formation. The results of this run
are plotted with solid lines. In both computational runs, mole fractions of boron and nitrogen elements within the mixture were the same, 45% and 55% respectively; pressure is atmospheric. This boron fraction was chosen arbitrary here; effect of boron fraction will be discussed in more details in the following section. Though full set of boron- and nitrogen-containing species was modeled, only densities of boron-containing species were affected by condensation. For the sake of keeping plots in the Figure 1 legible, only these species are shown; other species will be shown in following subsections. BN$_2$ molecules have very low densities compared to other species and are not plotted in Figure 1.

Figure 1. Effect of boron condensation on gas species densities in the B-N mixture. Solid lines – results obtained with accounting for the condensation; dashed lines – condensation not accounted for. Though full set of species was modeled, only densities of boron-containing species are affected by the condensation and plotted here. Condensation of boron has drastic effect on densities of all boron-containing gas species reducing their density by orders of magnitude. This effect is very important when determining gas species surrounding boron droplets at temperatures of solid BN formation.

From this figure it is clear that boron condensation has drastic effect on densities of all gas phase boron-containing species. When the gas mixture cools down and temperature reaches 4000 K, thermodynamics predicts that boron starts to condense, see line “Liquid B”, which shows density of boron atoms within liquid droplets in a unit gas volume. The condensation at definite temperature, can happen when the system becomes “oversaturated” in respect to the partial pressure of boron atoms. As a consequence of the formation of liquid boron, the amount of boron in the gas phase is lowered and the equilibrium density ratios among boron-containing species B, BN, B$_2$N, etc. in different gas phase reactions are disturbed. To reestablish this equilibrium, according to the Le Chatelier’s principle, the chemical reactions are shifted in direction of the formation of B atoms by additional dissociation of the boron-containing molecules, leading to the further formation of liquid boron until the
heterogeneous equilibrium between gas phase boron and liquid boron is completed. This also means that the partial pressure of boron atoms equals to its saturation level value, $p_B^s$ (which is a function of temperature, only); and solid line curve for B at T<4000K denotes the boron saturation vapor pressure curve. That value and thermodynamic equilibrium constants of chemical reactions determine the partial pressure values of other boron containing compounds BN, B_2N, B_2 etc. This question will be addressed in more detail in subsection III.G, where analytical relations for the species densities as functions of temperature are derived.

When temperature decreases to 3800 K, most of the boron has already condensed. When temperature approaches about 3000 K, thermodynamics predicts that formation of solid BN should begin, see line “Solid BN”. Because initially there was slightly more nitrogen than boron in the mixture, see also Figure 2, we can conclude that almost all liquid boron is consumed to form solid BN and some nitrogen is left in form of N_2 gas to maintain pressure within the system. Here and on subsequent figures, temperatures corresponding to initiation of boron condensation and formation of solid BN are marked in the figures with vertical grey lines.

Formation of solid BN involves, besides boron liquid, also nitrogen and boron containing gas phase species BN, B_2N etc. Their densities are determined by heterogeneous equilibrium and are considerably lower compared to those computed using one-phase procedure which does not take condensation of boron into account (denoted with dashed lines at T<4000K in Figure 1).

Note that Gibbs free energies for liquid boron and solid BN, which were used in present thermodynamic calculations, were obtained without accounting for surface energy effects for nanoparticles. They are valid for such relatively large volumes of liquid/solid that the surface effects can be neglected. However, at initial stage of condensation, when droplets of liquid boron nucleate and are very small (on a nanometer scale), the surface effect leads to a barrier for the nucleation of droplets. In the other words, while a gas mixture is cooling down, condensation does not immediately start when temperature reaches saturation point predicted by the thermodynamics. Calculations for aluminum and our calculations using NGDE code for boron have shown that no condensation happens until the actual gas pressure exceeds the saturated vapor pressure predicted by the thermodynamics about five times (i.e., the super saturation degree is about 5 instead of one) with a very weak dependence on a gas cooling rate. This supersaturation degree corresponds to the temperature of about 300 K below the saturation point for boron at atmospheric pressure (due to very strong dependence of vapor pressure on gas temperature). After that, nucleation and growth of boron droplets happens very rapidly, the surface energy effects for the droplets become negligible, the boron vapor condenses onto the droplets, equilibrium between gas and liquid phases is reached, and present thermodynamic predictions of the mixture compositions become valid.

In other words, the actual condensation temperature is about 300 K lower compared to the one predicted by thermodynamic calculations. In a shaded grey region denoted “Nucleation” in Fig. 1, the mixture is well described by the solution with no condensation (dashed lines). At the left boundary of
the shaded area mixture composition changes abruptly switching to the solution with condensation (solid lines).

Note that the main focus of this paper is determining the gas composition at temperatures corresponding to the formation of solid BN structures (e.g. nanotubes), these temperatures (2000-2400K; see Ref. [19]) are substantially lower than the temperature of boron condensation (∼4000 K; see Figure 1). The processes involved in the nucleation of boron droplets are out of the scope of this paper. Therefore, for the sake of simplicity of the subsequent figures, only thermodynamic results of the calculations considering liquid boron (solid lines in current notations) corresponding to gas in equilibrium with liquid are plotted.

III.B. Effect of pressure increase on the B-N mixture composition

In Figures 2, composition of B-N mixture is shown for pressures 1 atm. and 10 atm. Partial pressures of gas phase species are plotted as functions of temperature. N\textsubscript{3} molecules have low densities compared to other species and are not plotted. Temperatures of boron condensation and solid BN formation are shown with grey vertical lines. In order to show effect of boron fraction on the mixture composition, in addition to previously considered boron to nitrogen ratio 45 to 55, the results for a mixture with only 1% of boron are plotted. Apparently, reduction of the boron fraction affects boron partial pressure at higher temperatures, when no condensation takes place and all species are in the gas phase. As seen from the plots, it results in reduction of temperature at which boron vapor becomes saturated and condensation starts. At temperatures lower than that, fraction of boron in the gas phase and a chemical composition of the gas phase are generally determined only by the saturation vapor pressure and do not depend on the initial fraction of boron within the mixture. This result is also confirmed by analytical derivations presented in section III.G. Amount of boron in the liquid phase is obviously affected by its initial fraction; the initial amount of boron also affects the size of boron droplets formed during the condensation, as will be discussed in section III.F.

When boron starts condensing, molecular nitrogen, N\textsubscript{2}, becomes the major component in the mixture, with several orders of magnitude higher density than other components. N\textsubscript{2} molecules have high dissociation energy of 9.8 eV and can hardly be dissociated at boron droplets (unless they penetrate deep into boron\textsuperscript{19}); hence they are unlikely to be effective precursor for formation of B-N nanostructures. Among other nitrogen containing species, B\textsubscript{2}N has the highest density, an order of magnitude higher than its closest competitor, atomic N. This is due to its bond energy of about 6eV\textsuperscript{32}, B\textsubscript{2}N molecules can be disassembled at surfaces of boron droplets\textsuperscript{19} and can be suggested as major precursor for grows of BNNTs. Atomic nitrogen may contribute to the growth of BN nanostructures as well.
Interestingly, the increase of pressure from 1 atm. to 10 atm. resulted in increase of a factor of 3 of $B_2N$, possibly explaining an increase of nanotube production yield observed in Refs. [14] and [16].

![Graph showing composition of B-N mixtures at pressures 1 atm. (left) and 10 atm. (right) having boron to nitrogen ratios 45 to 55 (solid lines) and 1 to 99 (dotted lines). Boron condensation is taken into account; partial pressures of gas phase species are plotted as functions of temperature. Temperatures of boron condensation and solid BN formation are shown with vertical grey lines. Fraction of boron within the mixture affects composition of the gas species only at higher temperatures, before boron condensation starts. When the condensation takes place, gas species composition is determined merely by the boron vapor saturation curve. At the temperature of solid BN formation, $B_2N$ has the highest density among nitrogen containing species, after $N_2$, and can be suggested as major source of nitrogen for formation and growth of BNNTs. With the increase of pressure $p$, densities of $N$, $BN$ and $B_2N$ increased as $\sqrt{p}$ (as will be explained in subsection III.G), while the ratios between the species densities remained.](image)

**III.C. Effect of hydrogen addition**

Mixtures with 5% and 30% hydrogen addition at atmospheric pressure are considered. Results of the chemical composition computations are presented in Figures 3 and 4. Figure 3 has plots for densities of nitrogen-containing gas species. The rest gas species are shown in Figure 4. Note that $N_2H_2$ and $N_2H_4$ molecules were considered in the simulations but are not plotted because of their negligibly low densities.

As seen from Figure 3, even with substantial addition of hydrogen (30%), $B_2N$ is still major nitrogen-containing component (after $N_2$) at the moment when solid BN starts to form. Nevertheless, with further decrease of temperature, densities of all boron-containing species (including $B_2N$) continue to
drop rapidly, whereas density of ammonia NH$_3$ molecules grows. Soon, at temperature about 2600 K, NH$_3$ becomes major nitrogen-containing species, after N$_2$. NH and NH$_2$ molecules have much lower densities than NH$_3$ at these conditions. As shown in Ref. [57], molecules of ammonia dissociate at boron droplets and can effectively serve as feedstock of nitrogen for growth of solid BN structures. It is plausible that NH$_3$ molecules provide nitrogen for further growth of BNNTs at lower temperatures, when amount of B$_2$N molecules is significantly lowered due to condensation of boron, and boron droplet are not yet solid, which happens at temperature about 2350 K. In the other words, the addition of hydrogen might serve as a catalyst for extraction of nitrogen atoms from N$_2$ molecules which are at abundance at low temperatures, with their further incorporation in the growth of nanotubes. This might explain a higher yield production of longer nanotubes observed in the case of hydrogen addition$^{18}$.

Note that it is known that reaction of ammonia formation is slow at low temperatures due to activation energy. In order to speed up the reaction, iron catalyst and high pressure of about 200 atm are used for the ammonia production in well-known Haber-Bosch process$^{58}$. In this regard, it is questionable, whether NH$_3$ is produced fast enough in the nanosynthesis reactor to facilitate growth of the nanotubes. However, the Haber-Bosh process takes place at temperatures about 800 K, and temperatures of interest for the nanosynthesis above 2300 K. Activation energy for the NH$_3$ formation reaction is about 3 eV$^{58}$. This energy barrier plays crucial role at 800 K significantly slowing down the reaction, but it this effect might be much less pronounced at temperatures above 2300 K. Thorough answer to this question requires a separate research which is out of the scope of the present paper.

![Figure 3. Composition of B-N-H atmospheric pressure mixtures with hydrogen fractions of 5% (left) and 30% (right). Only nitrogen-containing species are plotted here (for other species, see Figure 4). Temperatures of boron condensation and solid BN formation are shown with vertical lines. With high hydrogen fraction, NH$_3$ molecules become prominent shortly after solid BN structures start to form and may serve as a nitrogen source for growth of BNNTs.](image-url)
Figure 4. Composition of B-N-H atmospheric pressure mixtures with hydrogen fractions of 5% (left) and 30% (right). Only species that do not contain nitrogen are plotted (for nitrogen-containing species, see Figure 3). Temperatures of boron condensation and solid BN formation are shown with vertical lines.

III.D. Comparison to OES data from Ref. [18]

In Ref. [18], high yield production of high quality BNNTs was achieved in ICP plasma reactor at atmospheric pressure with addition of up to 24% hydrogen to the gas mixture. Computational Fluid Dynamics (CFD) Simulations of gas flow with heat transfer were performed. Temperature and velocity profiles were obtained. Evaporation of BN powder and transport of BN vapor were simulated. Complete evaporation of the BN feedstock is suggested. However, chemical reactions within the system were not considered, BN gas was modeled as a non-reacting admixture, and gas mixture composition was not predicted in the modeling. Instead, optical emission spectra were measured at several locations within the reactor.

Simulations results\textsuperscript{18} on BN density and temperature allow us to estimate molar fraction of boron within the gas. The data\textsuperscript{18} on boron fraction and temperature can be used as an input for the thermodynamic modeling to compute the gas mixture compositions at given locations within the reactor. These results can be compared to OES data\textsuperscript{18}. The results for comparison are presented in Table 1.

First location where the spectrum was measured (0.38 m away from the inlet) had the gas temperature of about 5 000 K. BN gas molar fraction is about 2% meaning about 1% of boron molar fraction. NH molecular emission lines are prominent, N atoms and N\textsubscript{2} molecules were observed as well. Other
N-H-containing species such as NH$_2$ or NH$_3$ were not detected. Atomic B emission lines were detected as well as emission bands from BH and NH radicals. Spectral lines of atomic H were clearly identified, while the relative weakness of H$_2$ molecular band suggesting effective dissociation of H$_2$ into H atoms. A trace of BN molecules was observed but its intensity was much weaker than those of BH or NH radicals. These observations agree with the results of our thermodynamic modeling (see Figure 4). NH molecules have substantial density (molar fraction 10$^{-4}$ in case of high fraction of hydrogen within the mixture system), much higher than NH$_2$ and NH$_3$. Atomic boron has high density (molar fraction 0.02; almost all boron is in atomic form). B$_2$ and B$_3$ molecules have negligible fractions of below 10$^{-6}$. BH$_2$ and BH$_3$ molecules have densities of several orders of magnitude lower than BH. Hydrogen is mostly present in atomic form; density of H$_2$ molecules is about 3.5 orders of magnitude lower. Density of BN molecules is two orders of magnitude smaller than those of both BH and NH molecules.

| Location of the spectra measurement; gas temperature | Species detected in the OES spectra$^{18}$ | Species predicted by the thermodynamic modeling and their molar fractions |
|------------------------------------------------------|------------------------------------------|------------------------------------------------------------------------|
| Distance from the inlet: 0.38 m                      | Detected: N, N$_2$, NH, B, BH, H         | NH (3x10$^{-5}$), N (2x10$^{-2}$), N$_2$ (2x10$^{-4}$), B (2x10$^{-2}$), BH (3x10$^{-5}$), H (3x10$^{-5}$) |
| Temperature: 5 000 K                                | Weak signal: BN, H$_2$                    | BN (3x10$^{-7}$), H$_2$ (3x10$^{-3}$)                                  |
|                                                      | Not detected (as specified in Ref. [18]): N$_2$, NH$_2$, B$_2$, B$_3$ | NH$_2$ (10$^{-7}$), NH$_3$ (<10$^{-9}$), B$_2$ (3x10$^{-7}$), B$_3$ (<10$^{-9}$) |
| Distance from the inlet: 0.48 m                      | Detected: BH, H                           | BH (3x10$^{-6}$), H (3x10$^{-5}$)                                     |
| Temperature: 3 700 K                                | Not detected (as specified in Ref. [18]): B, NH | B (2x10$^{-2}$), NH (10$^{-5}$)                                      |
| Distance from the inlet: 0.88 m                      | Detected: H                              | H (10$^{-5}$)                                                         |
| Temperature: 2 400 K                                | Weak signal: BH                          | BH (3x10$^{-6}$)                                                      |
|                                                      | Not detected (as specified in Ref. [18]): B, NH | B (3x10$^{-8}$), NH (3x10$^{-8}$)                                    |

Table 1. Qualitative comparison between results of the OES measurements$^{18}$ and the thermodynamic modeling. Note that only the species that were specifically discussed in Ref. [18] as not observed by the OES are placed into the table as “not detected”. Good qualitative agreement is observed between the species densities predicted by the modeling and visibility of the species by the OES measurements.

At the next downstream locations where OES measurements were performed (0.48 m and 0.88 m from the inlet) corresponding to temperatures of 3700 K and 2400 K respectively, spectral lines of B atoms and NH molecules were no longer observed, whereas BH molecules and H atoms were still detected, and intensity of BH molecular band the most prominent at 0.48 m (3700 K). These observations agree well with the thermodynamic results (Figure 4): at temperatures of about 2400 K, density of H radicals...
is still high; it is of about the same order of magnitude as it was at 5000 K. Whereas, density of boron atom reduces about two orders of magnitude at 2400 K due to condensation of boron. Density of BH molecules at 3700 K is higher than at 5000 K, and at 2400 K is about the same as at 5000 K.

Note that in Ref. [18], enhanced growth of BNNTs in case of hydrogen addition to the gas mixture was attributed to presence of NH radicals in the mixture. It was assumed that BNNTs start to grow immediately when boron starts to condense, at temperature slightly below 4000 K, where density of NH radicals is high. However, results of thermodynamic modeling suggest that nanotubes and other solid BN structures start growing at temperatures below 2800 K where density of NH molecules is rather low, which is in agreement with the OES measurements. NH₃ molecules have higher density at these conditions, as discussed in a previous section.

III.E. Laser ablation of boron-rich targets: experimental setup and results

The sketch of the setup and the imaging on the iCCD is presented on Figure 5. The wavelength calibration was conducted with Hg and Xe calibration lamps: resulting diffusion relation was determined to be 0.18-0.16 Å/pixel and the instrumental width for slit with of 50 micron is ~1 Å. The experiments of laser ablation of BN target were conducted in a chamber in order to control the gas environment. Prior to the experiment the chamber was evacuated and subsequently filled with either He or N₂ gas, up to pressure of P=400 Torr. Details on the experimental setup are provided in appendix A.

The identification of atomic species was done according to the NIST database⁵⁹ and the molecular species – according to Refs. [60, 61]. Overall we have detected 3 band-heads of B₂N at 488.1, 504.3 and 519.5 nm [61], in experiments of BN target ablation in He and in N₂ environments. Figure 6 shows the temporal evolution of the spectrum in range 480-497 nm within the first microsecond after the laser pulse, in the experiment conducted in He-filled chamber. Presented spectra were captured with exposure of 50 ns, in 50 ns intervals, accumulating the emission from 100 shots. In order to show the temporal evolution in a single figure the intensity of each spectrum was normalized in the range (0, 1). The boron and nitrogen ion lines are prevalent in the spectrum, following the laser impact on the BN target. These lines are strongly broadened, owing to the high density and temperature in the spatial-temporal vicinity of the laser impact. After ~300 ns they disappear and the B₂N band emerges. The molecular B₂N emission bands were observed for tens of microseconds, after the laser shot. A more detail analysis of these results will be described in a separate paper. For the purpose of this work, the most important result is the observation of molecular species in the ablation plume which were also predicted by thermodynamic calculations.

To summarize, spectroscopic measurements verify presence of B₂N molecules in the B-N gas mixture at nearly atmospheric pressure. Interestingly, immediately following the laser pulse the B₂N molecules are not detected, only its precursors (B and N ions and atoms); it takes several fractions of microsecond
for $\text{B}_2\text{N}$ molecules to appear. This behavior supports the point that $\text{B}_2\text{N}$ molecules do not come directly from the target; they are formed by chemical reactions in the gas phase, as suggested by the thermodynamic modeling.

Figure 5. Experimental setup in laser ablation experiment of $\text{BN}$ target.

Figure 6. Temporal evolution of the spatially-integrated, ablation spectrum of solid $\text{BN}$ in He ($P=400$ Torr), in the 480-497 nm range. The intensities were normalized in 0-1 range in order to show the spectra on the single plot.
III.F. Estimation of boron droplets size upon formation of BNNTs in an ICP and arc discharge reactors

Growth of boron droplets can be divided in two stages\(^{51}\): 1) the nucleation stage refers to a statistical process of boron atoms aggregation into clusters in which stable boron droplets are formed; 2) the agglomeration stage refers to a process of droplets growth via collisions with each other leading to their coagulation into larger droplets.

In a cooling gas mixture, nucleation of droplets does not happen immediately when conditions for the gas condensation are met as predicted by thermodynamics. This is due to energy barrier to the formation of stable droplets\(^{51}\). For boron, the “delay” is about 300 K, with a very weak dependence on the gas cooling rate. When this condition on the temperature is met, nucleation happens abruptly, and many stable droplets are rapidly formed. Once the droplets are formed, their growth can be described using a simple agglomeration theory\(^{62}\). This theory was applied in Ref. [35] to describe growth of carbon nanoparticles, and good agreement on the size of particles with results of in-situ measurements\(^{63}\) was obtained. Initial size of nucleated particles is very small (containing tens of atoms\(^{56}\)) compared to grown particles and can be neglected. With this simplification, a relation for average diameters of the nanoparticles reads\(^{35}\):

\[
D = \left(2r_0\right)^{9/5} n_0^{3/5} \left(\frac{4\pi kT}{m_B}\right)^{1/5} T_t^{2/5}.
\]  

Here, \(t\) is time elapsed from the beginning of particles agglomeration, \(r_0 \approx 1.2 \times 10^{-10} m\) is Wigner-Seitz radius for boron describing distance between atoms in a boron droplet, \(n_0\) is density of boron atoms in the gas at the beginning of condensation, \(k\) is Boltzmann constant, \(m_B\) is mass of boron atom and \(T\) is temperature.

Constant temperature is assumed in (10), which is not exactly the case for a cooling gas, however, typically temperature variation between nucleation of boron droplets and formation of BNNTs is rather small (about 20%-30%), and temperature is raised to a small power (10). Hence, temperature variation can be neglected for simplicity, and average temperature \(T = 0.5\left(T_{nucl} + T_{end}\right)\) can be used in (10) resulting in a very small error. Here, \(T_{nucl}\) is predict temperatures at which nucleation of boron droplets takes place and agglomeration initiates, which can be predicted by thermodynamics for a gas mixture with a given molar fraction of boron (300 K should be subtracted to account for the nucleation energy barrier). \(T_{end}\) is final temperature at which size of the nanoparticles should be determined. With a constant cooling rate \(\dot{T}_0\), (10) can be transformed:

\[
D = \left(2r_0\right)^{9/5} n_0^{3/5} \left(\frac{4\pi k\left(T_{nucl} + T_{end}\right)}{m_B}\right)^{1/5} \left(\frac{T_{nucl} - T_{end}}{\dot{T}_0}\right)^{2/5}.
\]  

Here, \(T_{nucl}\) is predict temperatures at which nucleation of boron droplets takes place and agglomeration initiates, which can be predicted by thermodynamics for a gas mixture with a given molar fraction of boron (300 K should be subtracted to account for the nucleation energy barrier). \(T_{end}\) is final temperature at which size of the nanoparticles should be determined. With a constant cooling rate \(\dot{T}_0\), (10) can be transformed:
$T_{\text{end}}$ can be taken equal to temperature at which formation of BNNTs and other solid BN structures takes place, $T_{\text{BNNT}}$, if size of boron droplet upon formation of BNNTs is of interest. Alternatively, $T_{\text{end}}$ can be taken equal to the temperature of boron solidification, $T_{B_{\text{solid}}}$, if final size of boron droplets is of interest.

In the ICP reactor\(^\text{18}\), pressure is 1 atm. and molar fraction of boron is about 1\% yielding nucleation temperature of $3500K$ and solid BN formation temperature $T_{\text{BNNT}} = 2800K$, according to the thermodynamic computations (see Figures 2 and 4). Temperature of boron solidification is $T_{B_{\text{solid}}} = 2300K$\(^\text{31}\). Due to energy barrier for the nucleation, actual nucleation temperature is $300K$ lower than one predicted by the thermodynamics: $T_{\text{nuc}} = 3200K$. For these temperature and boron molar fraction, density of the boron vapor is: $n_0 \approx 3 \times 10^{22} m^{-3}$. Cooling rate $\dot{T}_0$ is about $6 \times 10^4 K/s$ (according to Ref. [18], flow velocity is about 20 m/s and temperature gradient is 3000 K/m in the region of interest) in the case with hydrogen addition, when BNNTs are produced. Substitution of these parameters into (11) yields diameter of the boron droplets upon formation of BNNTs of about 20nm. It is difficult to validate this value experimentally, \textit{in-situ} measurements diameter of boron droplets diameters amidst the flight, when nanotubes grow on them, would be required. However, validation of this model can be performed by comparing final the size of boron droplets predicted by (11) to \textit{ex-situ} TEM images of boron droplets with no nanotubes produced in the case without addition of hydrogen (see Figure 3f in Ref. [18]). In the no-hydrogen case, cooling rate was about $10^5 K/s$ (velocity 20 m/s and temperature gradient about 5000 K/m). Substitution of this value and $T_{B_{\text{solid}}}$ in (11) yield final diameter of boron droplets of about 20nm (coincidentally, the same as for boron droplets with nanotubes grown with the addition of hydrogen). As seen from the TEM image\(^\text{18}\), there were mainly boron particles of $15 nm - 20 nm$, that is in a good agreement with our theoretical prediction.

The same method can be applied to assess size of boron droplets in the electric arc reactor for BNNT synthesis\(^\text{12}\). Unfortunately, no quantitative data is available on boron molar fraction and gas cooling rate within the nanoparticle growth region in electric arc in nitrogen for synthesis of BNNTs. However, for general assessment, analogy with a carbon arc studied in Ref. [35] can be employed here: both arcs have similar size and power, in both arcs one of the electrodes ablates, and evaporated material (boron or carbon) diffuses in surrounding gas to the nanoparticles growth region. This approach makes sense because the results of (11) are weakly dependent on the input parameters. In Ref. [35], simulations predicted coincidently the same parameters as in ICP system\(^\text{18}\): molar fraction of the ablated material in the growth region about 1\%, and cooling rate $\dot{T}_0$ about $2.5 \times 10^5 K/s$. This yields diameter of boron droplets of about 10nm–15nm. This result is in an agreement with \textit{ex-situ} TEM image of boron droplets with nanotubes grown on them (see Figure 3 in Ref. [12]). Again, these are just order of magnitude estimates, for more accurate predictions, modeling of the arc with in nitrogen for BNNT synthesis is required.
III.G. Analytical relations for species densities

In the thermodynamic approach, densities of species are determined via minimization of relation (7) with constraints (5) and (6). Note that in (7), densities of various species are substantially different, by many orders of magnitude. Apparently, species with higher densities have higher impact on chemical composition of other species within the system. Having this in mind, relation (7) can be substantially simplified when determining density of any particular species. For any species of interest, only species with major densities having the same chemical elements need to be considered.

For instance, when considering atomic nitrogen, only diatomic nitrogen $N_2$ needs to be kept in equation (7) as a dominant nitrogen-containing species. This yields following relation for densities of $N$ and $N_2$:

\[
\sum_{i \in N, N_2} N_i \left( kT \left( \ln N_i - \ln \left( \sum_{k \in N, N_2} N_k \right) + \ln \frac{P}{P_0} \right) + G_i \left( P_0, T \right) \right) \rightarrow \text{min},
\]

with following constraint:

\[
N_N + 2N_{N_2} = N_N'.
\]

Here, $N_N$ is number if nitrogen atoms, $N_{N_2}$ is number of nitrogen diatomic molecules, and $N_N'$ is total number of nitrogen atoms in all species within the system (is constant), $P_0 = 1 \text{ atm.}$ is a reference pressure for which the Gibbs energies of formation $G_i^f$ are determined for various species $i$, as introduced in eq. (2).

Solution of (12) and (13) yields following relation:

\[
\frac{N_{N_2} \left( N_{N_2} + N_N \right)}{N_N^2} = \frac{P}{P_0} \exp \left( \frac{\Delta G_N}{RT} \right),
\]

where $\Delta G_N = 2G_N' \left( P_0, T \right) - G_{N_2}' \left( P_0, T \right)$; $G_N$ and $G_{N_2}$ are energies of formation for $N$ and $N_2$ respectively. Or, in terms of species densities (using relation (8)):

\[
\frac{n_{N_2} \left( n_{N_2} + n_N \right)}{n_N^2} = \frac{P}{P_0} \exp \left( \frac{\Delta G_N}{RT} \right).
\]

This relation is known as the law of mass action\textsuperscript{36,64} for a dissociation reaction. Taking into account that $N_2$ is the major component in the mixture within temperature range considered, and its partial
pressure is roughly equal to the total gas pressure $p$, the following relation for partial pressure of atomic nitrogen is obtained:

$$p_N = \sqrt{P_0 p} \exp \left( \frac{\Delta G_N}{2RT} \right).$$

(14)

As for boron, major boron containing species within the mixture is either its atomic gas phase at higher temperatures or its liquid phase at lower temperatures. In order to find densities of these two species, equation (7) can be simplified to:

$$N_B \left( RT \ln \frac{P}{P_0} + G_B \right) + N_{B,l} G_{B,l} \rightarrow \min,$$

(15)

with following constraint:

$$N_B + N_{B,l} = N_B^*.$$  

(16)

Here, subscripts $B$ and $B,l$ refer to atoms in gas and liquid states respectively. Solution of (15) and (16) yields following relation for partial pressure of atomic boron gas:

$$p_B = P_0 \min \left( \exp \left( \frac{-\Delta G_B}{RT} \right), x_{B,max} \right).$$

(17)

Here, $\Delta G_B = G_B^f \left(p_0, T\right) - G_{B,l}^f \left(T\right) + RT$, and $x_{B,max} \approx 2b_B$ is maximum molar fraction of boron gas (when all boron is in gas phase). Factor “2” before $b_B$ is to take into account that boron is mostly present in atomic form and nitrogen – in form of N$_2$ molecules:

$$x_{B,max} \approx \frac{N_B}{N_B + N_{N_2}} \approx \frac{N_B^*}{N_B^* + N_{N_2}^*/2} = \frac{2b_B}{1 + b_B} \approx 2b_B.$$

Relation (17) is similar to a known Clausius-Clapeyron equation for saturation pressure, but formulated in terms of Gibbs free energies.

Knowing densities and pressures of major nitrogen (N$_2$) and boron (B) gas species allows determining densities of B-N compound molecules $B_x N_y$. For such molecules, equation (7) can be written in a simplified form similar to (12), with summation over three species: $B$, $N_2$ and $B_x N_y$. Following constraints on the species densities should be applied:

$$N_B + xN_{B,N_y} = N_{B,ST},$$

$$2N_{N_2} + yN_{B,N_y} = N_N^*.$$  

(18)
Here, \( N_{\text{g,s}}^* \) is total number of boron atoms in the gas phase, which is determined by condensation of boron and, hence, is conserved on conversion of \( N_{\text{B,N_2}} \) into other gas species. Both \( N_{\text{g}}^* \) and \( N_{\text{B,g}}^* \) can be considered constants in (18). Solution of this system in a general case is rather bulky; however, taking into account that \( N_{\text{B,N_2}} \ll N_{\text{N_2}}^* \) and usually \( N_{\text{B,g}}^* < N_{\text{N_2}}^* \), compact solution can be written:

\[
N_{\text{B,N_2}} = \left( N_{\text{B}}^* \right)^x \left( \frac{N_{\text{N_2}}^*}{2} \right)^{1-x} \left( \frac{p}{p_0} \right)^{\frac{y}{2} + x - 1} \exp \left( -\frac{\Delta G}{RT} \right),
\]

or, formulated in terms of partial pressures, taking into account that \( N_2 \) is major component in the mixture:

\[
p_{\text{B,N_2}} = \left( p_B \right)^x \left( \frac{p}{p_0} \right)^{\frac{y}{2} + x - 1} \exp \left( -\frac{\Delta G}{RT} \right).
\]  

(19)

Here, \( \Delta G = G_{\text{B,N_2}}^{f} \left( p_0, T \right) - xG_{\text{B}}^{f} \left( p_0, T \right) - \frac{y}{2} G_{\text{N_2}}^{f} \left( p_0, T \right) \). \( p_B \) in (19) can be taken as predicted by (17).

For temperatures below saturation point of boron this yields:

\[
p_{\text{B,N_2}} = \frac{p_B^x}{p_0^y} \exp \left( -\frac{\Delta \tilde{G}}{RT} \right),
\]  

(20)

where \( \Delta \tilde{G} = G_{\text{B,N_2}}^{f} \left( p_0, T \right) - \frac{y}{2} G_{\text{N_2}}^{f} \left( p_0, T \right) - xG_{\text{B,H}}^{f} (T) - xRT \).

Eq. (20) can be considered as a generic equation boron and nitrogen containing species \( \text{N, BN, B}_2\text{N, B, B}_2 \) and \( \text{N}_2 \) corresponding to different values of \( x \) and \( y \). Typically, \( \Delta \tilde{G} \) has linear dependence on temperature. In this regard, Eq. (20) can be rewritten in Arrhenius form:

\[
p_{\text{B,N_2}} = p_B^x p_0^{\frac{y}{2}} A_{\text{B,N_2}} \exp \left( -\frac{T_{\text{B,N_2}}}{T} \right).
\]  

(21)

Similar relations can be derived for hydrogen-containing species \( \text{H, B}_x\text{H}_y \) and \( \text{N}_x\text{H}_y \), for temperatures below 3200 K, where \( \text{H}_2 \) is major hydrogen-containing component (see Figures 3, 4). For convenience, let’s formulate it in a general form, for species \( \text{B}_x\text{N}_y\text{H}_z \) (\( x, y \) and \( z \) can be zero). The relation for the partial pressure as a function of Gibbs free energy change takes a form:
\[
p_{B_{x}N_{y}H_{z}} = p^\frac{y+z}{2} p_0^{1-\frac{y+z}{2}} \exp \left( -\frac{\Delta \hat{G}}{RT} \right),
\]

where \( \Delta \hat{G} = G_{B_{x}N_{y}H_{z}}^f (p_0, T) - xG_{B_{x}}^f (p_0, T) - \frac{y}{2} G_{N_{y}}^f (p_0, T) - \frac{z}{2} G_{H_{z}}^f (p_0, T) - xRT \).

This yields following Arrhenius form for the partial pressure of \( B_{x}N_{y}H_{z} \) species:

\[
p_{B_{x}N_{y}H_{z}} = p^\frac{y+z}{2} p_0^{1-\frac{y+z}{2}} A_{B_{x}N_{y}H_{z}} \exp \left( -\frac{T_{B_{x}N_{y}H_{z}}}{T} \right),
\]

(22)

Values of coefficients \( A_{B_{x}N_{y}H_{z}} \) and \( T_{B_{x}N_{y}H_{z}} \) for various species are summarized in Table 2.

| Species, \( B_{x}N_{y}H_{z} \) | \( A_{B_{x}N_{y}H_{z}} \) | \( T_{B_{x}N_{y}H_{z}}, K \) |
|-----------------|----------------|------------------|
| B               | 515 000        | 58 800           |
| \( B_2 \)       | 1 962 000      | 81 900           |
| \( B_3 \)       | 238 000        | 74 100           |
| N               | 3 600          | 58 100           |
| \( N_3 \)       | 2.9x10^{-3}    | 51 700           |
| BN              | 359 000        | 65 000           |
| \( B_2N \)      | 535 000        | 40 700           |
| H               | 1 570          | 27 500           |
| BH              | 5 300          | 44 000           |
| \( BH_2 \)      | 5.2            | 15 400           |
| \( BH_3 \)      | 7.2x10^{-4}    | 2 780            |
| NH              | 11.5           | 45 400           |
| \( NH_2 \)      | 7.1x10^{-3}    | 22 400           |
| \( NH_3 \)      | 9.7x10^{-7}    | -6 100           |

Table 2. Coefficients \( A_{B_{x}N_{y}H_{z}} \) and \( T_{B_{x}N_{y}H_{z}} \) for various species in Eq. (22) for the species densities.

Pressures of B atoms, \( N_2 \), BN and \( B_2N \) molecules obtained with formulas (14), (17) and (19) are plotted in Figure 7 as functions of temperature, in comparison with results of full thermodynamic solution for the B-N mixture. As seen from the Figure, at temperatures above the point of solid BN formation, simple algebraic relations (14), (17) and (19) provide pretty accurate values without the
need to perform numerical minimization of relation (7). It enables quick analysis of the mixture composition and determination which species are present when BNNTs and other BN structures start to form.

Figure 7. Partial pressures of selected species obtained using algebraic relations (14), (17) and (19) as functions of temperature (dotted lines), in comparison with results of full thermodynamic modeling of the B-N mixture (solid lines). 45% boron and 55% nitrogen within the mixture, two pressures are considered. Good agreement between full modeling results and analytical solutions is observed for temperatures higher than point of solid BN formation.

Conclusions

Calculations of equilibrium chemical composition for B-N mixture with and without addition of hydrogen at 1 atm. and 10 atm. in the temperature range between 1000K and 6000K were performed using thermodynamic approach. A broad set of species was considered including BN, B₂N and BN₂ gas phase molecules, liquid boron and solid BN. Latest allowed accounting for condensation of boron and determining conditions at which formation of solid BN structures take place, which can be interpreted as conditions for growth of BNNTs. The thermodynamic calculations predict that in a cooling mixture, boron condenses at first providing seed particles for the growth of BNNTs to grow, supporting “root growth” mechanism. It was shown that condensation of boron has drastic effect on the gas phase composition yielding reduction of boron-containing species densities by several orders of magnitude at temperatures corresponding to the formation of boron liquid (droplets) and BNNTs. This effect was not considered in previous thermodynamic studies of B-N mixtures and should be taken into account when studying conditions for growth of BNNTs.
Results of the thermodynamic calculations have shown that B$_2$N molecules have the highest density among nitrogen-containing species, after N$_2$, when BNNTs grow on surface of boron droplets. Unlike B$_2$N molecule, N$_2$ has high dissociation energy and can hardly dissociate on a boron surface in order to contribute to the formation of periodic B-N structure within BNNT. Hence, B$_2$N molecules can be suggested as major source of nitrogen for formation and growth of BNNTs. These predictions are supported with experimental results obtained by our OES measurements during laser ablation of boron-rich target. Atomic nitrogen can give some contribution to the growth as well. Other nitrogen-containing species have much lower densities and cannot have substantial impact on the growth of BNNTs.

The results of the thermodynamic calculations were also verified by qualitative comparison to spectroscopic measurements of the gas composition at several locations within the ICP plasma reactor of Ref. [18]. Measured spectral line intensities of several species (N, N$_2$, NH, B, BH, H, BN, H$_2$) at three locations in the ICP plasma reactor qualitatively agree with predictions by the thermodynamic calculations.

Effect of the pressure increase from 1 atm. to 10 atm. on the gas composition was studied. It was shown that because density of boron gas is determined merely by the saturation curve and does not depend on the background pressure, densities of N, BN and B$_2$N molecules increase proportionally to square root of pressure. These results suggest that precursors for formation of BNNTs remain the same (B$_2$N molecules and N atoms), and enhanced production yield and purity of BNNTs observed in Refs. [14] and [16] at higher pressures can be attributed to increase of densities of these precursors.

Convenient analytical relations in Arrhenius form (22) were derived to describe species densities at various pressures and temperatures higher than point of solid BN formation. Values of coefficients for the Arrhenius expression for various species were provided.

References [17] and [18] observed enhanced BNNT production with hydrogen addition. Our thermodynamic calculations show that formation of NH$_3$ molecules at temperatures of BNNT formation might be responsible for this effect, because NH$_3$ molecules provide nitrogen impingent into boron droplets and hence enhance BNNT growth.

We calculate the size of boron droplets where BNNTs grow. Boron gas density, temperature and flow velocity were taken from the fluid modeling. Good agreement between our simulation results and observed in ex-situ TEM photos for the droplets size was obtained. It was shown that the initial fraction of boron in the system does not affect composition of the gas mixture when BNNTs grow, because most of boron condenses into liquid droplets (though the initial fraction of boron affects size of boron droplets on which the BNNTs grow, see Eq. (10)).
Appendix A. Details on the experimental setup for laser ablation of boron-rich targets and OES measurements

Laser ablation is driven by Nd:Yag laser (Surelite III-10), equipped with second and third harmonic generators. The laser produced pulses of 1064 nm wavelength at frequency of 10 Hz, which are converted to 355 nm, by the frequency conversion unit. The emerging laser has a full-width-at-half-maximum (FWHM) duration of ~7 ns. The laser beam was guided into the investigation area and focused on the target with lens (f=300 mm). The target is boron-nitride (BN) tablet, having diameter of 25 mm and a height of 5 mm. The BN target was held in a 3D-printed pedestal, which in turn was connected to a rotation motor. Fast rotation of the target prevents the dipping of the laser into the target. The resulting ablation plume is imaged with a lens on the entrance of the imaging spectrometer (iHoriba 550). The entrance slit of the spectrometer was set to a width of 50 microns and the spectrometer grating of 1200 groves/mm was employed to diffuse the light. An iCCD camera (PI-MAX 3, 1024x1024 pixel CCD) is connected to the exit port of the spectrometer for detection. A Dove prism located between the lens and the spectrometer slit rotates the image by 90°. In this fashion the ablation plume was imaged on the iCCD vertically: the target was on the top of the CCD, the plume is extended from top to bottom and horizontal direction on the iCCD corresponds to different wavelengths.

Acknowledgements

The authors would like to thank Dr. Predrag Krstic (Stony Brook University), Dr. Longtao Han (Stony Brook University), Dr. Rachel Selinsky (Princeton University), Dr. Roberto Car (Princeton University), Dr. Biswajit Santra (Princeton University) and Dr. Andrei Khodak (PPPL) for fruitful discussions. The thermodynamic modeling was supported by the US Department of Energy (DOE), Office of Science, Fusion Energy Sciences. Laser ablation experiments and nanoparticle growth calculations were supported by the US DOE, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division.
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