CREATING A DETAILED MODEL FOR BORON NITRIDE DEPOSITION MECHANICS

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Abstract

This work sets out to create a validated mechanism to model the deposition of boron nitride films in low pressure chemical vapor deposition reactors. A model proposed by Mark Allendorf et al. at Sandia National Laboratories, published in 1996 acts as a starting point for an expanded model. The program Reaction Mechanism Generator (RMG) from MIT is being used to theoretically expand the model. Boron will be added into this program to achieve this goal. The Gaussian program is also used to generate thermochemical data for various intermediate species that is required for RMG. Once an expanded boron nitride mechanism is created, the model will be validated experimentally with a micro-chemical vapor deposition reactor used in tandem with a gas chromatograph to sample species data within the reactor at various initial conditions. This work remains ongoing.

Introduction

It is well documented that ceramic matrix composite (CMC) materials, especially those based on carbon and silicon-carbide fibers, offer some of the highest strengths at temperatures over 1000 °C (Fig. 1), but crack formation at fiber-matrix interfaces and subsequent oxidation/corrosion of CMCs have posed major reliability issues at high temperatures of relevance for NASA applications. One solution to this problem is to coat these composites in an interface material to allow for some increased flexibility and slip between different fiber tows, and generally act as a reinforcement to the matrix.[2] One common interface coating that has been studied in previous literature is boron nitride (BN).[2,3] BN is a good interface material because it forms a weak mechanical bond and has minimal reactions with many CMCs.[2] This prevents the BN from damaging the CMC while providing the overall matrix increased flexibility and toughness. While BN has been used to increase survivability of CMCs, no current mechanisms exist that model the formation of BN and/or BN intermediate species.

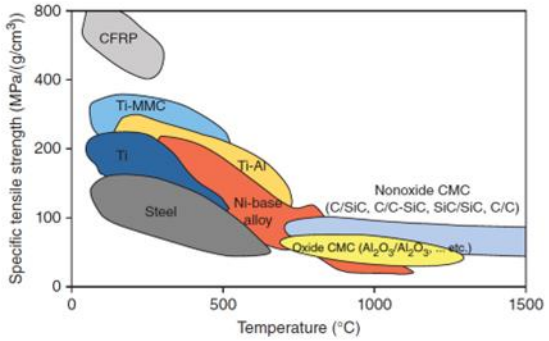

Figure 1: weight specific strength materials as a function temperature.[1] (adapted from Ref. 1)

The main method of forming BN films is via Chemical Vapor Infiltration (CVD). As BN and doped-BN films are becoming more common, it is becoming increasingly necessary to understand and model flow compositions in various reactor conditions in order to maximize production and film quality. A detailed model would also help researchers understand the many intermediate reactions that play a role in BN deposition.

Literature Review

Currently, there is one published, semi-global mechanism detailed in Allendorf et al. that contains 11 reactions pertaining to BN formation via boron trichloride (BCl_3) and ammonia (NH_3).[4] These two species are common precursors to BN formation, and have been used for BN deposition since the 1960s.[5-9] Despite the large number of applications and studies of BN for the last 80 years, the Allendorf model remains the only published mechanism, though it only contains eleven reactions. Some reaction rates were also estimated in the high-pressure limit for increased accuracy, though BN is typically grown in low-pressure CVD reactors.

Other mechanisms related to BN (i.e., pertaining to elements B-Cl-N-H) have also been proposed and tested. Though Allendorf's model predicts that BCl_3 decomposition is largely negligible at common CVD reactor conditions (less than 5% decomposition below 1400K with one second residence time),[4] such pathways may become more important at higher operating conditions. A model proposed by Reinisch et al. describes reactions within a boron/hydrogen/chlorine/carbon system.[10] Select reactions from this model pertaining to B/H/Cl reactions may prove important in the expansion of current BN deposition understanding. Similarly, Shrestha et al. describes reactions within a nitrogen/hydrogen/carbon/oxygen system.[11] In this case, reactions involving N/H can be used to help expand the model.

Methodology

To build a working mechanism to model BN deposition, both theoretical and experimental approaches are necessary. First, the theoretical model must be expanded upon to estimate species concentrations within CVD reactors. Then, when predicted stable and measurable species are identified from the model, a gas chromatograph can be used with a CVD reactor to measure actual species concentrations within any range of input parameters. Then, various reactions within the model can be tuned to better reflect the reality displayed within the CVD reactor. Once the model has been tested and validated, the model may be reduced to a one-step model for implementation into various CFD simulation software.

Initially, the Allendorf model had to be compiled into a working CTI-style format. In various appendices, the thermochemical data (thermodata), given in the NASA 14-coefficient style to describe specific heat, enthalpy, and entropy, was found and compiled into the CTI file. This data was originally calculated in a separate paper by Allendorf and Melius in 1997 using the BAC-MP4 method.[12] While many other relevant species have been well documented in their thermochemical and transport data, such as BCl_3 and NH_3, the intermediate species must be studied theoretically, as they are unstable and thusly cannot be studied in traditional, experimental manners. As such, the thermodata for select intermediate species was first compared to new data generated with the Gaussian program (described in more detail in the following section) using a similar level of theory.

Theoretical Modeling

Gaussian is a program that allows the user to perform various computational chemistry calculations based on theoretical atomic and molecular data.[13] To properly utilize Gaussian's ability to calculate specific heat, enthalpy, and entropy data, reasonable bond lengths and angles are needed to represent the species of interest. For various intermediate species for the B-Cl-N-H system, Reinhardt et al. has published this necessary values.[14] The bond lengths and angles are calculated at the second-order Møller–Plesset perturbation theory (MP2) level.

Seen below in Figures 3-5 is a comparison between the specific heat, enthalpy, and entropy calculations between Allendorf's data

	Reaction	ΔH°_{reac} [f]	A [h]	E_a	Notes
1.	$Cl_3BNH_3 \leftrightarrow BCl_3 + NH_3$	24.0	--	--	f
2.	$Cl_3BNH_3 \leftrightarrow Cl_2BNH_2 + HCl$	11.1	--	--	f
3.	$BCl_3 + NH_3 \leftrightarrow Cl_2BNH_2 + HCl$	-12.9	1.66E+12	19.9	a,b
4.	$Cl_2BNH_2 \leftrightarrow ClBNH + HCl$	56.0	3.89E+14	79.0	a,b,c
5.	$Cl_2BNH_2 + NH_3 \leftrightarrow BCl(NH_2)_2 + HCl$	-3.9	1.66E+12	19.9	a
6.	$BCl(NH_2)_2 + NH_3 \leftrightarrow B(NH_2)_3 + HCl$	6.9	1.66E+12	19.9	a
7.	$BCl_3 \leftrightarrow BCl_2 + Cl$	117.7	9.86E+15	113.7	a,c,d
8.	$BCl_2 \leftrightarrow Cl + BCl$	79.7	2.25E+15	76.9	a,c,d
9.	$BCl_3 + H \leftrightarrow BCl_2 + HCl$	14.5	1.00E+14	12.0	a
10.	$BCl + HCl \leftrightarrow BCl_2 + H$	23.4	7.23E+13	24.2	e
11.	$NH_3 + M \leftrightarrow NH_2 + H + M$	109.1	2.50E+16	93.8	g

[a] This work. [b] Transition state from Ref. [9]. [c] High-pressure limit. [d] Rate estimated by RRKM calculation. [e] Ref. [16]. [f] Ref. [9], kcal mol^{-1}, 298 K. [g] Ref. [11]. [h] Units: cm, sec, moles.

Figure 2: Semi-empirical gas-phase mechanism for BN from Allendorf et al.[4]

and Gaussian's theoretically generated data. The blue lines represent data generated from MP2//cc-pVTZ level theory in Gaussian, and the orange line is Allendorf's data using BAC-MP4 theory.

Enthalpy values needed to be converted from Gaussian's energy calculations. To do this, the enthalpy of formation of each intermediate species was needed. This was calculated using steps in a paper from Ochterski in 2000.[15] Equations 1-3 detail how this can be done.

$$\Delta H_f^\circ(M,0K) = \sum_{atoms} x\Delta H_f^\circ(X,0K) - \sum D_0(M) \quad (1)$$

$$D_0(M) = \sum_{atoms} x\, \mathcal{E}_0(X) - \mathcal{E}_0(\mathrm{M}) - \mathcal{E}_{ZPE}(M) \quad (2)$$

$$\Delta H_f^\circ(M,298K) = \Delta H_f^\circ(M,0K) + \left(H_M^\circ(298K) - H_M^\circ(0K)\right) - \sum_{atoms} x(H_X^\circ(298K) - (H_X^\circ(0K)) \quad (3)$$

In this process, it was discovered that small changes in the values of element-specific data, such as its element of formation, can cascade to larger changes in the enthalpy of formation. This then effects the location of the enthalpy line, shown in Figure 4. Table 1 lists values for boron's enthalpy of formation compared to the later enthalpy of formation for BCl_3 and BCl_2.

Table 1: Enthalpies of formation for boron, and the associated enthalpies of formation for BCl_3 [kcal/mol].

B	BCl_3	BCl_2
132.62 (16)	-108.024	-15.641
136.20 (17)	-104.444	-12.061
133.80 (18)	-106.844	-14.461
138.10 (19)	-102.544	-10.161

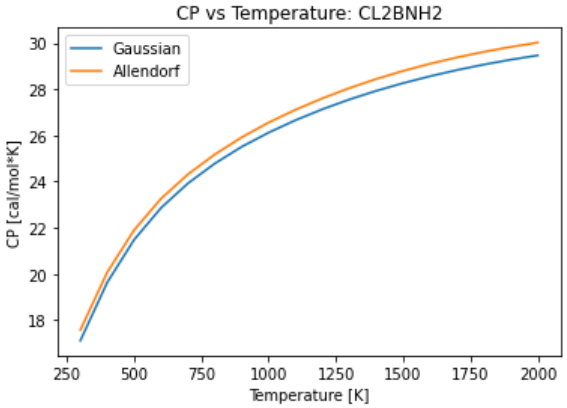

Figure 3: Specific heat versus temperature for the Cl_2BNH_2 intermediate species.

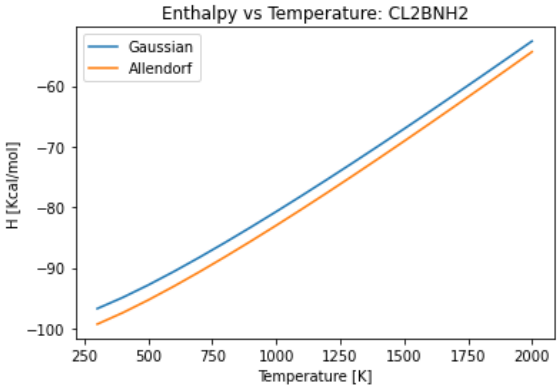

Figure 4: Enthalpy versus temperature for the Cl_2BNH_2 intermediate species.

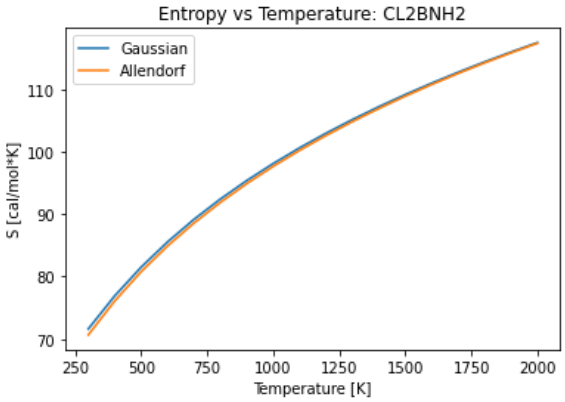

Figure 5: Entropy versus temperature for the Cl_2BNH_2 intermediate species.

Further analysis of the effects of the elemental data on larger species data calculations, reaction enthalpies, and the importance of data documentation is present in an upcoming conference presentation and paper at the 2023 JANNAF meeting.

With the data confirmed to be accurate to more recent calculations, the next step of the project was to begin expanding the Allendorf model. A program that is currently being used for this is Reaction Mechanism Generator (RMG) developed by research groups with William Green at MIT and Richard West at Northeastern University.

RMG is a powerful open-source program that allows users to generate theoretical chemical kinetic models which are composed of various elementary reaction steps.[20] It does this by combining general knowledge on how atoms and molecules react with each other and various preexisting databases for thermodynamic, transport, and kinetic data. RMG has the ability to learn from preexisting kinetic families, used as 'training' data, and can optimize models given various input parameters. RMG currently offers support of most row 1 and row 2 elements of the periodic table and selected heavier elements (H, He, C, N, O, F, Ne, Si, S, Cl, Ar, Br, I). Boron is not present in this list, so to use this program, boron is currently being manually added into the program.

Adding boron into RMG requires the addition of various types of data. A group at the Indian Institute of Technology started similar work with boron to produce an improved model for boron carbide (BC).[21] In corresponding with Dr. Vijay Shinde, the methodology to add boron into RMG was obtained. Necessary information to add includes the bonding modes for boron, elemental properties, various thermodynamic data for different stable and radical species containing boron, adding a limb on the existing species tree structure (which organizes and groups the species into different 'branches' such as nesting two-bond species under BX_2. An example of this tree structure is given in Figure 6. For any species which are not coded into RMG but 'created' by the program, Benson group additivity theory is used to estimate thermodynamic properties.[22]

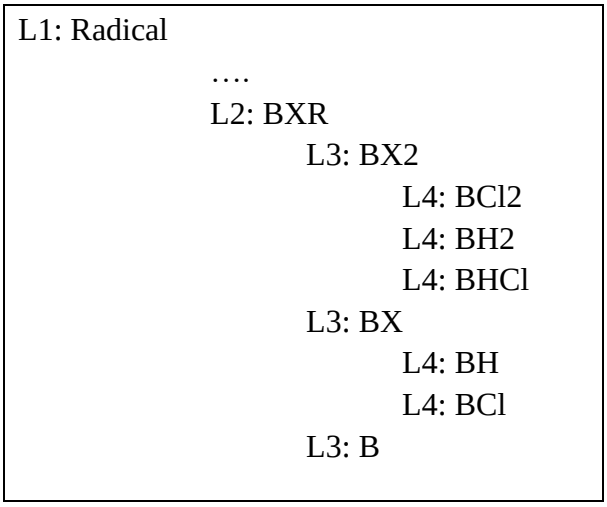

Figure 6: Possible tree structure addition for radical boron species, with similarly bonded species nesting together.

As mentioned, RMG has the ability to learn from pre-existing datasets which can be input into the source code. Such datasets are uploaded as both reaction libraries and reaction families. Libraries simply act as repositories of potential reactions which RMG can choose to include, but families are unique in that they allow RMG to 'learn' from preexisting reaction types and extrapolate new reactions from them. From Dr. Shinde, examples pertaining to the BC work were obtained. Currently, preliminary results show that boron has been properly added into the system. The goal of the next theoretical steps is to recreate the model generated by Gupta et al. with BC, and then to

look forward to adding both the Allendorf model into the libraries/families and including various boron-nitrogen containing species into the thermochemical data trees.

Experimental Work

To validate any boron nitrogen model that comes from the theoretical investigation, a low-pressure CVD reactor has been built. Figure 7 shows a schematic of the reactor setup. The reactor's temperature profile has been confirmed to be constant at various target temperature profiles, seen in Figure 8. The constant temperature is crucial to proper model validation. In the rig, reaction times can be measured by varying residence time in the reactor. This will allow species measurements by the gas chromatograph (GC) at various times (with the reactor length being constant), and thus species data at various times can be plotted. Pressure has also been maintained at target values of 10 Torr. The experiment is in the end stages of being tested, and testing of the Allendorf model can begin. Validation of the

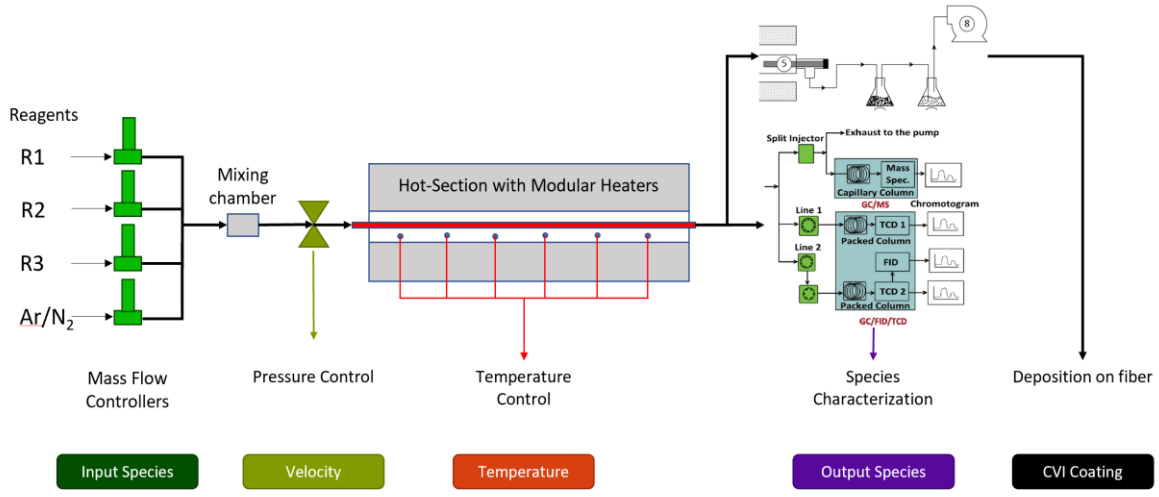

Figure 7: CVD reactor setup. Flow is from left to right.

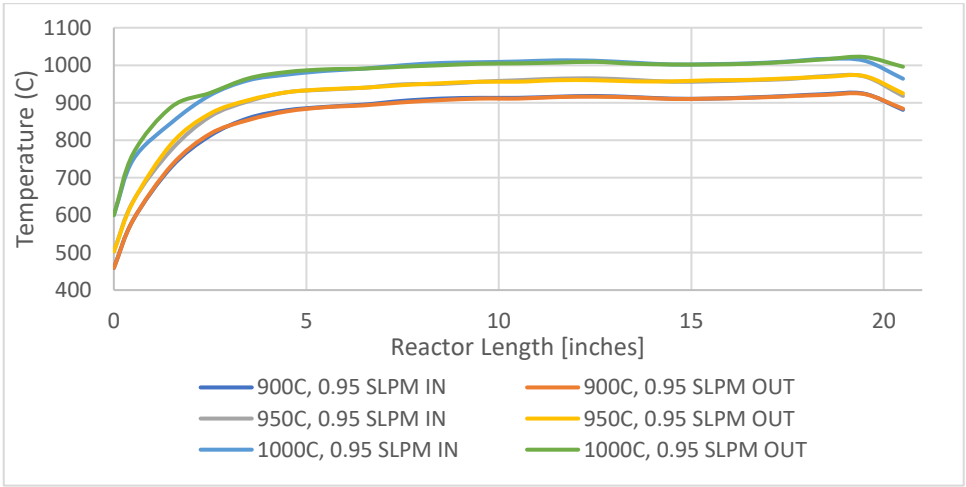

Figure 8: Confirmation of constant temperature throughout reactor. Sample location and gas sampling at around 18.5 inches.

results from the RMG-generated model will begin as well. No speciation data has been collected from the GC yet, but two test cases have successfully deposited boron nitride films onto quartz substrates. Figure 9a and 9b show results from the second test case.

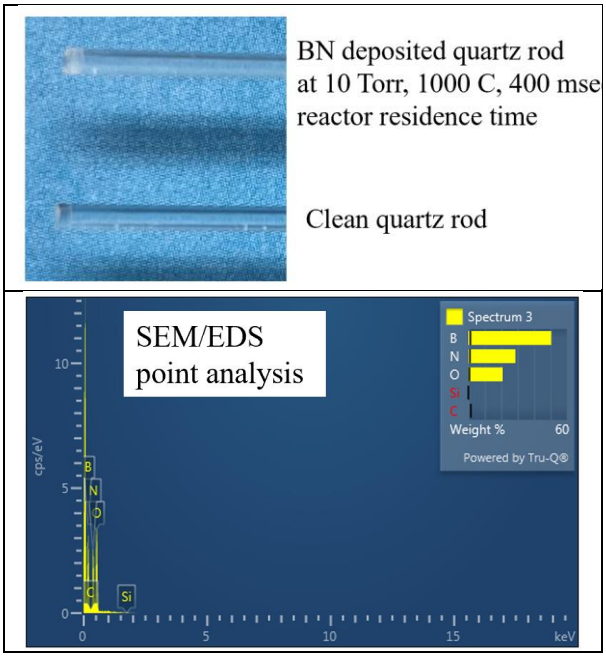

Figure 9: (a) Quartz rod with BN film compared to a clean rod. (b) SEM/EDS point analysis of BN film on SiO_2 rod.

Figure 9b shows a new 1:1 ratio of B:N, indicating success in depositing a thin-film BN layer. Oxygen reading is likely due to the point-analysis and sensing some of the quartz surface. More testing will improve the quality of this layer (B:N ratio) and thus the success of the model validation.

Future Work

Once boron is confirmed to be successfully added into RMG with the BC model, the RMG dataset will be expanded to include various boron-nitrogen containing species in the thermochemistry section, and the Allendorf model will be added for RMG to use in theoretical model generations. The CVD reactor will then be used to sample species data at various initial conditions to validate and 'tune' the model where necessary. Once an expanded model for BN is ready, steps for reducing the model to one-step for implementation into various computational fluid dynamics software will be created.

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References

[1] Bernhard Heidenreich, Andreas Kienzle, "Carbon Fiber Reinforced Ceramic Composites, Industrial Carbon and Graphite Materials," in Industrial Carbon and Graphite Materials (eds.), Volume I, 10.1002/9783527674046, (825-884), (2021).

[2] Arthur W. Moore and Michael Dowell, "Interface Coating for Ceramic Fibers," US Patent no. 5,593,728, (1997).

[3] Li, Qin, Liu, Ye, Li, Cheng, and Zhang, "Effect of the SiCl4 Flow Rate on SiBN Deposition Kinetics in SiCl4-BCl3-NH3-H2-Ar Environment," in Materials, doi: 10.3390/ma10060627, (2017).

[4] M. D. Allendorf, C. F. Melius, and T. H. Osterheld, "A Model of the Gas-Phase Chemistry of Boron Nitride CVD from BCl3 and NH3," in Covalent Ceramics III – Science and Technology of Non-Oxides, Volume 410, (1996).

[5] N. Patibandla and K. L. Luthra, "Chemical Vapor Deposition of Boron Nitride'" in Journal of The Electrochemical Society, Volume 139, No. 12, (1992).

[6] Basche, M., & Schiff, D. (1964). New pyrolytic boron nitride. *Mater. Des. Eng*, *59*(2), 78-8l.

[7] Pierson, H. O. (1975). Boron Nitride Composites By Chemical Vapor Deposition*. *Journal of Composite Materials228*, *9*(3), 228–240.

[8] J. L. Hurd, D. L. Perry, B. T. Lee, K. M. Yu, E. D. Bourret andE. E. Haller.,J.Mater.Res., 1989,4, 350

[9] Carminati, P., Buffeteau, T., Daugey, N., Chollon, G., Rebillat, F., & Jacques, S. (2018). Low pressure chemical vapour deposition of BN: Relationship between gas phase chemistry and coating microstructure. *Thin Solid Films*, *664*, 106–114. https://doi.org/10.1016/j.tsf.2018.08.020

[10] Guillaume Reinisch, Gérard L. Vignoles, and Jean-Marc Leyssale, "Reaction Mechanism for the Thermal Decomposition of BCL3/CH4/H2 Gas Mixtures," in Journal of Physical Chemistry, dx.doi.org/10.1021/jp2039114, (2011).

[11] Krishna P. Shrestha, Lars Seidel, Thomas Zeuch, and Fabian Mauss, "Detailed Kinetic Mechanism for the Oxidation of Ammonia Including the Formation and Reduction of Nitrogen Oxides," in Energy & Fuels, doi.org/10.1021/acs.energyfuels.8b01056

[12] Allendorf, M. D., Melius, C. F. (1997) Thermochemistry of Molecules in the B-N-Cl-H System: Ab Initio Predictions using the BAC-MP4 Method. *J. Phys. Chem. A*, 101,2670-2680

[13] About Gaussian 16. Gaussian, https://gaussian.com/g16main/

[14] Reinhardt, S., Gastreich, M., & Marian, C. M. (2000). Reactions in the initial stage of the CVD of BN - A quantum chemical investigation. *Physical Chemistry Chemical Physics*, *2*(5), 955–963. https://doi.org/10.1039/a908247f

[15] Ochterski, J. W. (2000). *Thermochemistry in Gaussian*.

[16] Chase, M. NIST-JANAF Thermochemical Tables, 4th Edition. American Institute of Physics, -1, 1998-08-01 1998

[17] Storms, E., and Mueller, B. Phase relations and thermodynamic properties of transition metal borides. i. the molybdenum-boron system and elemental boron. The Journal of Physical Chemistry 81, 4 (1977), 318–324.

[18] Cox, J. D., Wagman, D. D., and Medvedev, V. A. Codata key values for thermodynamics, 1989.

[19] Searcy, A. W., and Myers, C. E. The heat of sublimation of boron and the gaseous species of the boron–boric oxide system. The Journal of Physical Chemistry 61, 7 (1957), 957–960.

[20] Gao CW, Allen JW, Green WH, West RH. Reaction mechanism generator: automatic construction of chemical kinetic mechanisms. *Comput Phys Commun.* 2016:203:212–25.

[21] A Gupta, S Nigam, VM Shinde, Gas-phase kinetic of boron carbide chemical vapor deposition using BCL3+CH4+H2 mixtures, *J. Am. Ceramic Soc.* 105:3885-3895 (2022).

[22] S. W. Benson, Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters 2d ed., John Wiley & Sons, New York, 1976.