Machine learning and a computational fluid dynamic approach to estimate phase composition of chemical vapor deposition boron carbide

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Received: August 10, 2020; Revised: December 24, 2020; Accepted: January 6, 2021

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Abstract: Chemical vapor deposition is an important method for the preparation of boron carbide. Knowledge of the correlation between the phase composition of the deposit and the deposition conditions (temperature, inlet gas composition, total pressure, reactor configuration, and total flow rate) has not been completely determined. In this work, a novel approach to identify the kinetic mechanisms for the deposit composition is presented. Machine learning (ML) and computational fluid dynamic (CFD) techniques are utilized to identify core factors that influence the deposit composition. It has been shown that ML, combined with CFD, can reduce the prediction error from about 25% to 7%, compared with the ML approach alone. The sensitivity coefficient study shows that BHCl_2 and BCl_3 produce the most boron atoms, while C_2H_4 and CH_4 are the main sources of carbon atoms. The new approach can accurately predict the deposited boron–carbon ratio and provide a new design solution for other multi-element systems.

Keywords: machine learning (ML); computational fluid dynamic (CFD); chemical vapor deposition; boron carbide; B/C ratio; kinetic mechanisms

1 Introduction

Ceramic matrix composites (CMC) are ideal high-temperature materials because of their high-temperature resistance, wear resistance, low thermal conductivity,

low thermal expansion coefficient, high chemical resistance, and high strength [1,2]. The common material systems of CMC are carbon fiber-reinforced silicon carbide matrix composite, carbon fiber-reinforced carbon matrix composite, and silicon carbide fiber-reinforced silicon carbide matrix composite (C_f/SiC , C_f/C , and SiC_f/SiC) [3,4]. Because boron carbide (B_xC) can react with oxygen to generate boron oxide glass phase (B_2O_3 , HBO_3 , and H_3BO_3) and then seal cracks to

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prevent further oxidation [5–9], it is a good candidate for oxidation protective materials, and it is usually added to modify the interface and matrix of CMC.

Chemical vapor deposition (CVD) is a promising method for the preparation of boron carbide [7,10–12]. The deposition mechanism for B_xC from a $BCl_3-CH_4-H_2$ system has been previously studied. For instance, Berjonneau *et al.* [13,14] identified the main gaseous species *in situ* by Fourier transform infrared (FTIR) spectroscopy, such as BCl_3 , $BHCl_2$, and HCl . The B/C ratio of the deposits decreased from 3.6 to 2 when the deposition temperature increased from 900 to 1100 °C. Karaman *et al.* [11,12] considered $BHCl_2$ a by-product of the gas phase. Liu *et al.* [15] systematically studied the relationship between deposition morphology and processing conditions. They found that temperature has an effect on the phase composition and microstructure. At higher temperatures (1050–1100 °C), the deposits consisted of two interlaced phases (PyC and boron carbide) with low boron content ranging from about 40 to 49 at%. At lower temperatures (900–950 °C), layered and dense B_4C was produced with uniform phase composition, and its boron content is 65–79 at%.

It was considered that B_xC exists as a single stable phase in a large homogeneous region from about 8 to 20 at% carbon concentration (the corresponding B/C ratio is from 11.5 to 4) [7], and then a carbon-rich B_xC coating was obtained when B/C ratio was lower than 4 [15,16]. Thus, it is important to elucidate the correlation between the B/C ratio of the deposit and the deposition conditions to achieve reproducibility and consistency in the process. Apart from experimental studies, some numerical studies have provided an in-depth understanding of deposition kinetics [17–19], but scarce modeling attempts have been reported in boron carbide. Only Reinisch *et al.* [20] reported it by combining experimental and reaction kinetics computations, and brought strong evidences of the presence of methyldichloroborane (MDB, BCl_2CH_3) in the process.

This paper is concerned with the correlation between deposit composition and processing parameters, such as temperature, inlet gas concentration, pressure, and gas flow velocity. A novel approach that considers gas phase kinetics and heat and mass transfer, in combination with machine learning (ML), is proposed to better understand the actual deposition mechanism and design of the deposit composition. The approach was applied to a $BCl_3-CH_4-H_2$ system, which provides a useful foundation in understanding other precursor systems, such as

$SiCl_4-BCl_3-NH_3-H_2-Ar$ [21] and $BCl_3-MTS-H_2$ [13].

This paper is organized as follows: In Section 2, the details of the reactor model (RM) and two machine learning (ML) methods, including error back propagation (BP) algorithm and support vector machine (SVM), are presented. In Section 3, ML was used to directly correlate the global processing parameters (temperature, inlet gas composition, total pressure, reactor inner diameter, and total flow rate) with the experimentally measured boron–carbon ratio of the deposits. However, no satisfactory functional relationship was found. Then, the proposed method was applied and validated by comparing the experimental data.

2 Model simulation and prediction

2.1 Reactor-scale model

The experimental data reported by Berjonneau *et al.* [13,14] and Liu *et al.* [15] are adopted in this study. The specific deposition parameters for their experiments are listed in Table 1. In Ref. [15], B_4C and pyrolytic carbon (PyC) were deposited onto graphite slices (30 mm × 15 mm × 2 mm) [15]. Boron trichloride ($BCl_3 \geq 99.99$ vol%) and methane ($CH_4 \geq 99.95$ vol%) were used as the boron and carbon sources, respectively. The reactor was a vertical, hot-wall deposition furnace with a 200 mm inner diameter (a diagram of the equipment is shown in Fig. 1). The temperature within the reactor was 900–1100 °C, and the pressure was fixed at 10 kPa. Berjonneau *et al.* [13,14] adopted the analogous CVD reactor, which was a vertical silica glass tube (700 mm in length and 34 mm in internal diameter) heated in its central part by a radio-frequency induction furnace. Their processing conditions are as follows: 850–1000 °C, 2–12 kPa, and total flow rate of 210–390 sccm.

Because the reactor is cylindrical and symmetrical, its CFD model can be simplified to a two-dimensional axisymmetric model. The mass and heat transfer values were accounted via conservation of mass and conservation of momentum:

$$\nabla \cdot (\rho \mathbf{u}) = 0 \quad (1)$$

$$\rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \left[-p\mathbf{I} + \mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu(\nabla \cdot \mathbf{u})\mathbf{I} \right] \quad (2)$$

where p is the total fluid pressure, μ is the hydrodynamic viscosity, ρ is the fluid density, $\mathbf{u}$ is the fluid velocity field, and $\mathbf{I}$ is the unit tensor.

Table 1 CVD experimental conditions from Refs. [13–15]

No.	T (°C)	Q (sccm)	ID (mm)	P (kPa)	In_BCl ₃	In_CH ₄	In_H ₂	B/C
1	900	125	200	10	10/23	2/23	11/23	4.34
2	900	125	200	10	2/19	2/19	15/19	0.31
3	900	125	200	10	2/5	2/15	11/15	4.70
4	950	125	200	10	8/23	2/23	13/23	2.31
5	950	125	200	10	4/15	2/15	9/15	1.83
6	950	125	200	10	8/21	2/21	11/21	0.99
7	1000	125	200	10	2/11	2/11	7/11	0.35
8	1000	125	200	10	4/19	2/19	13/19	0.42
9	1000	125	200	10	10/27	2/27	15/27	2.32
10	1050	125	200	10	6/17	2/17	9/17	0.91
11	1050	125	200	10	4/19	2/19	13/19	0.70
12	1050	125	200	10	8/19	2/19	9/19	0.84
13	1100	125	200	10	6/23	2/23	15/23	0.78
14	1100	125	200	10	10/19	2/19	7/19	0.98
15	1100	125	200	10	2/15	2/15	11/15	0.44
16	850	250	34	12	4/25	1/25	20/25	3.5
17	900	250	34	12	4/25	1/25	20/25	2.8
18	950	250	34	12	4/25	1/25	20/25	2.8
19	850	390	34	12	2/13	1/13	10/13	3.6
20	900	390	34	12	2/13	1/13	10/13	3.0
21	950	390	34	12	2/13	1/13	10/13	3.2
22	1000	390	34	12	2/13	1/13	10/13	2.0
23	850	390	34	12	4/13	1/13	8/13	2.9
24	900	390	34	12	4/13	1/13	8/13	3.1
25	950	390	34	12	4/13	1/13	8/13	2.6
26	850	210	34	12	2/7	1/7	4/7	2.4
27	900	210	34	12	2/7	1/7	4/7	2.3
28	950	210	34	12	2/7	1/7	4/7	2.9

Note: Q is the total flow rate. In_BCl₃, In_CH₄, and In_H₂ are the input molar fractions of BCl₃, CH₄, and H₂, respectively. ID is the reactor inner diameter and B/C is the boron–carbon ratio of the deposited products.

Fig. 1 CVD reactor equipment diagram.

The chamber was heated through the induction of the graphite layer by the radiation frequency (RF) coil

to generate eddy currents. Heat transfer occurred mainly through surface radiation and convection conduction, and the electromagnetic phenomenon was neglected. The main governing equations are as follows:

$$\rho C_p \mathbf{u} \cdot \nabla T + \nabla \cdot \mathbf{q} = Q \quad (3)$$

where C_p is the fluid heat capacity, T is the deposition temperature of the fluid, and q is the Fourier heat conduction. The radiative transfer equation (RTE) is used to describe the transfer process of radiant heat.

A beam of incident light propagates in the medium along the Ω direction and interacts with the medium. Part of the light intensity $I(\Omega)$ is partially absorbed by $kI(\Omega)$, where k (m^{−1}) is the absorption coefficient; the other part of the light is along $\sigma_s I(\Omega)$ direction

scattering, where $(\sigma_s, \text{m}^{-1})$ is the scattering coefficient. The intensity of directional light will be attenuated by scattering in different directions, and will be enhanced by radiation in different directions. Therefore, this radiation process is described by the following equation:

$$\Omega \cdot \nabla I(\Omega) = kI_b(T) - (k + \sigma_s)I(\Omega) + \frac{\sigma_s}{4\pi} \int_0^{4\pi} I(\Omega') \phi(\Omega', \Omega) d\Omega' \quad (4)$$

where the probability of ray scattering from the direction of Ω' to the direction of Ω is described by the scattering phase function $\phi(\Omega', \Omega)$. kI_b represents the radiation of the medium in all directions, where I_b is the intensity of the black body.

The most commonly used method for calculating the radiation transfer equation is the discrete coordinate method. The principle of this method is to calculate the ordinate component in the discrete direction. Therefore, it is still necessary to solve the intensity I by calculating the partial differential equation on each discrete ordinate:

$$S_i \cdot \nabla I_i = kI_b(T) - (k + \sigma_s)I_i + \frac{\sigma_s}{4\pi} \sum_{j=1}^n \omega_j I_j \phi(S_j, S_i) \quad (5)$$

where S_i is the discrete ordinate in the i -th direction and ω_j is the orthogonal weight.

For multi-component diffusion, the balance of the i -th chemical species includes the contribution of diffusion, convection, and loss/production of species in K gas phase reactions.

$$\frac{\partial(\rho w_i)}{\partial t} = -\nabla \cdot (\rho \omega_i \vec{v}) - \nabla \cdot \vec{J}_i + M_i \sum_{k=1}^K v_{ik} (\mathfrak{R}_k^g - \mathfrak{R}_{-k}^g), \quad i = 1, \dots, N \quad (6)$$

Among them, ω_i and M_i represent the mass fraction and molecular weight of species i , respectively. The total mass and mole fraction are

$$\sum_{i=1}^N \omega_i = 1 \quad (7)$$

$$\sum_{i=1}^N x_i = 1 \quad (8)$$

Diffusion flux ($\vec{J}_i$) is the sum of concentration ($\vec{J}_i^c$) and temperature gradient ($\vec{J}_i^T$):

$$\vec{J}_i = \vec{J}_i^c + \vec{J}_i^T \quad (9)$$

$$\vec{J}_i^T = -D_i^T \frac{\nabla T}{T}, \quad i = 1, \dots, N \quad (10)$$

$$\vec{J}_i^c = -\sum_{j=1}^N (\rho D_{ij}) \nabla \omega_j, \quad i = 1, \dots, N \quad (11)$$

where D_{ij} and D_i^T are the matrix of multi-component diffusion coefficient and multi-component thermal diffusion coefficient, respectively. D_i^T is calculated by gas kinetic theory, and specific information can be found in Ref. [22]. The following equation was used to calculate the binary diffusion rate (m^2/s) [23]:

$$D_i = 1.8829 \times 10^{-32} \frac{\sqrt{T^3 (M_A + M_B) / (M_A M_B)}}{p \sigma_{AB} \Omega_D} \quad (12)$$

where M is the molar mass, σ is the minimum energy value of the characteristic length; subscripts A and B indicate binary diffusion gas species; and Ω_D is the collision integral:

$$\Omega_D = f\left(T, \sigma, \frac{\varepsilon}{k_b}, \mu_D\right) \quad (13)$$

To calculate the collision integral Ω_D , we need to define the minimum energy values of the characteristic length and Lennard–Jones interaction potential, which are σ (10^{-10} m) and ε/k_b (K), respectively. It is also necessary to provide a material dipole moment μ_D (Debye). The values were obtained from Ref. [24], databases, or experiments (Table 2). σ and ε/k_b of BCl_3 were approximated for the unknown coefficients of other boron-containing intermediates.

The density of the mixed gas is expressed by the ideal gas equation:

$$\rho = \frac{PM}{RT} \quad (14)$$

$$M = \sum_{i=1}^N x_i M_i \quad (15)$$

where M is the molar mass of the mixed gas.

Table 2 Characteristic lengths of major substances ε/k_b and Lennard–Jones interaction potential (σ)

Gas species	ε/k_b (K)	σ (Å)
CH_4	154	3.78
C_2H_2	209	4.1
C_2H_4	280	3.97
C_2H_6	252.3	4.302
HCl	344.7	3.339
H_2	38	2.92
BCl_3	337.7	5.127

Note: The material dipole moment μ_D is uniformly zero.

The detailed chemical kinetic model that describes gas-phase reactions in CVD has been presented in several studies. Table 3 lists 62 reversible reactions adopted for the gas model in the present case. Ge *et al.* [25–27] focused precisely on the thermodynamics of Si–C–H–Cl systems. Moreover, the temperature conditions they studied are within the range of our research temperature. Therefore, for C–H–Cl systems (G1–G44 in Table 3), we preferentially adopted Ge's

calculated data. Based on the most favorable reaction path previously proposed, Liu *et al.* [28] studied the reaction rate of the $\text{BCl}_3/\text{CH}_4/\text{H}_2$ gas-phase system. Their rate constants were calculated for temperatures within 200–2000 K and adopted G45–G58 [29]. Reinisch *et al.* [30] reported a set of theoretical experiments of the gas-phase decomposition of boron trichloride in the presence of hydrogen radicals, and their reactions are also included (G59–G62 in Table 3).

Table 3 A list of gas phase reaction models

No.	Reaction	A (s^{-1} or $\text{m}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$)	n	E ($\text{kJ}\cdot\text{mol}^{-1}$)
G1	$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$	8.3×10^{13}	0	434.4
	Reverse rate	1.294×10^9	−0.4	0
G2	$\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	5.317×10^{11}	0.892	454.7
	Reverse rate	430.4	1.273	271.2
G3	$\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	1.66×10^{13}	0.093	171.5
	Reverse rate	9.834×10^7	0.098	30.1
G4	$\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3$	1.2×10^{22}	−1.79	381
	Reverse rate	1.024×10^9	−0.64	0
G5	$\text{C}_2\text{H}_6 + \text{CH}_2 \leftrightarrow \text{C}_2\text{H}_5 + \text{CH}_3$	1.2×10^8	0	0
G6	$2\text{CH} \leftrightarrow \text{C}_2\text{H}_2$	1.204×10^8	0	0
G7	$\text{CH}_2 + \text{H} \leftrightarrow \text{CH} + \text{H}_2$	3.011×10^7	0	0
G8	$\text{CH}_2 + \text{CH} \leftrightarrow \text{C}_2\text{H}_2 + \text{H}$	3.975×10^7	0	0
G9	$2\text{CH}_2 \leftrightarrow \text{C}_2\text{H}_4$	1.024×10^6	0	0
G10	$2\text{CH}_2 \leftrightarrow \text{C}_2\text{H}_2 + 2\text{H}$	1.084×10^8	0	3.3
G11	$2\text{CH}_2 \leftrightarrow \text{C}_2\text{H}_2 + \text{H}_2$	1.204×10^7	0	3.3
G12	$\text{CH}_3 + \text{CH} \leftrightarrow \text{C}_2\text{H}_3 + \text{H}$	3.011×10^7	0	0
G13	$\text{CH}_3 + \text{CH}_2 \leftrightarrow \text{C}_2\text{H}_4 + \text{H}$	1.807×10^7	0	0
G14	$2\text{CH}_3 \rightarrow \text{C}_2\text{H}_5 + \text{H}$	1.148×10^{15}	0	110
	Reverse rate	3.674×10^7	0	0
G15	$\text{CH}_4 + \text{CH} \leftrightarrow \text{C}_2\text{H}_5$	1.626×10^8	0	0
G16	$\text{CH}_4 + \text{CH} \leftrightarrow \text{C}_2\text{H}_4 + \text{H}$	3.011×10^7	0	−1.6
G17	$\text{CH}_4 + \text{CH}_2 \leftrightarrow \text{C}_2\text{H}_6$	1.024×10^7	0	0
G18	$\text{C}_2\text{H}_3 + \text{M} \leftrightarrow \text{C}_2\text{H}_2 + \text{H} + \text{M}$	3.011×10^9	0	133
G19	$\text{C}_2\text{H}_3 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	3.011×10^{-2}	2.63	36
	Reverse rate	1.325	2.53	51
G20	$\text{C}_2\text{H}_3 + \text{CH}_2 \leftrightarrow \text{C}_2\text{H}_2 + \text{CH}_3$	1.807×10^7	0	0
G21	$\text{C}_2\text{H}_3 + \text{CH}_3 \leftrightarrow \text{C}_2\text{H}_2 + \text{CH}_4$	3.914×10^5	0	0
G22	$\text{C}_2\text{H}_4 + \text{M} \leftrightarrow \text{C}_2\text{H}_2 + \text{H}_2 + \text{M}$	1.5×10^9	0	233.6
G23	$\text{C}_2\text{H}_4 + \text{M} \leftrightarrow \text{C}_2\text{H}_3 + \text{H} + \text{M}$	1.4×10^{10}	0	344.8
G24	$\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_5 + \text{H}$	1.024×10^7	0	285
	Reverse rate	1.807×10^6	0	0
G25	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_2 \leftrightarrow 2\text{C}_2\text{H}_3$	2.409×10^7	0	286
G26	$2\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3 + \text{C}_2\text{H}_5$	4.818×10^8	0	299
	Reverse rate	4.818×10^5	0	0
G27	$\text{CH}_4 + \text{CH}_3 \leftrightarrow \text{C}_2\text{H}_5 + \text{H}_2$	1.024×10^7	0	95.6

(Continued)

No.	Reaction	A (s^{-1} or $m^3 \cdot mol^{-1} \cdot s^{-1}$)	n	E ($kJ \cdot mol^{-1}$)
G28	$C_2H_5 + H_2 \rightarrow C_2H_6 + H$	3.071×10^{-6}	3.6	35
	Reverse rate	1.445×10^3	1.5	31
G29	$C_2H_5 + CH_3 \leftrightarrow C_2H_4 + CH_4$	1.987×10^7	0.5	0
G30	$C_2H_6 + CH_3 \rightarrow C_2H_5 + CH_4$	0.549×10^{-3}	4	34.6
	Reverse rate	8.618×10^{-8}	4.14	52.6
G31	$2C_2H_5 \leftrightarrow C_2H_6 + C_2H_4$	7.227×10^6	0	4.5
G32	$C_2H_5 + C_2H_4 \rightarrow C_2H_6 + C_2H_3$	6.624×10^{-4}	3.13	75.4
	Reverse rate	6.022×10^{-4}	3.3	43.9
G33	$C_2H_2 + C_2H_6 \rightarrow C_2H_3 + C_2H_5$	104.4	2.05	292.8
	Reverse rate	5.553×10^7	-0.346	46.4
G34	$C_2H_4 \rightarrow C_2H_3 + H$	4.365×10^{12}	0.945	451.6
	Reverse rate	8.428×10^7	0	0
G35	$2CH_3 \rightarrow CH_2 + CH_4$	0.0152	3.153	64.6
	Reverse rate	62.25	2.451	54.8
G36	$CH_2 + HCl \rightarrow CH_3 + Cl$	183.417	1.71	8.9
	Reverse rate	39.6	2.24	31.8
G37	$CH_3 + Cl \rightarrow CH_2 + HCl$	2.2×10^7	0	34.5
	Reverse rate	1.698×10^6	0	3.63
G38	$C_2H_5 + HCl \rightarrow C_2H_6 + Cl$	0.0123	2.29	0
	Reverse rate	1.4365×10^4	1.476	8.4
G39	$CH_3 + HCl \rightarrow CH_4 + Cl$	70.106	1.412	15.7
	Reverse rate	1.642×10^{-7}	4.51	5.9
G40	$H_2 + H \rightarrow 3H$	2.228×10^8	0	402
	Reverse rate	9.792×10^5	-1	0
G41	$2H_2 \rightarrow 2H + H_2$	9.033×10^8	0	402
	Reverse rate	9.792×10^4	-0.6	0
G42	$2H + M \leftrightarrow H_2 + M$	5.44×10^{12}	-1.3	0
G43	$HCl \rightarrow H + Cl$	1.109×10^{17}	-0.681	417.6
	Reverse rate	96.39	1.87	-35.2
G44	$Cl + H_2 \rightarrow HCl + H$	7.52×10^{-4}	3.39	-4.9
	Reverse rate	4.379×10^8	-0.091	35.4
G45	$BCl_3 \rightarrow BCl_2 + Cl$	5.85×10^{13}	0.31	464.1
	Reverse rate	2.74×10^8	1.44	17.88
G46	$CH_4 + BCl_3 \rightarrow CH_3BCl_2 + HCl$	2.08×10^7	1.43	194.8
	Reverse rate	2.4×10^8	0.5	148.4
G47	$CH_3BCl_2 \rightarrow CH_2BCl_2 + H$	1.98×10^8	1.6	348.2
	Reverse rate	4.29×10^8	1.23	12.7
G48	$CH_3BCl_2 + Cl \rightarrow CH_2BCl_2 + HCl$	8.67×10^6	1.79	5.43
	Reverse rate	1.76×10^6	1.78	53.0
G49	$CH_2BCl_2 \rightarrow CHBCl_2 + H$	1.5×10^{16}	-0.79	218.75
	Reverse rate	6.2×10^{15}	-0.87	55.4
G50	$CHBCl_2 + H \rightarrow CHBCl + HCl$	1.05×10^9	1.36	38.58
	Reverse rate	4.6×10^5	2.16	127.6
G51	$CHBCl + Cl \rightarrow CBCl + HCl$	2.67×10^{14}	-0.48	247.49
	Reverse rate	6.4×10^{11}	0.048	159.2

(Continued)

No.	Reaction	A (s^{-1} or $m^3 \cdot mol^{-1} \cdot s^{-1}$)	n	E ($kJ \cdot mol^{-1}$)
G52	$CBCl + H \rightarrow CHBCl$	4.58×10^{11}	0.89	2.69
	Reverse rate	1.05×10^{25}	0.77	18.61
G53	$CHBCl \rightarrow BC + HCl$	7.0×10^{13}	-0.024	30.12
	Reverse rate	1.17×10^8	1.64	39.2
G54	$BCl_3 + H_2 \rightarrow BHCl_2 + HCl$	1.26×10^9	1.11	191.3
	Reverse rate	2.24×10^4	2.13	99.65
G55	$BHCl_2 + H \rightarrow BH_2Cl_2$	3.29×10^9	1.28	7.15
	Reverse rate	3.52×10^{25}	0.58	0.98
G56	$BH_2Cl_2 \rightarrow BCl_2 + H_2$	2.25×10^{15}	-0.69	54.83
	Reverse rate	6.68×10^9	0.47	64.8
G57	$BCl_2 \rightarrow BCl + Cl$	1.90×10^{12}	0.47	305.5
	Reverse rate	1.4×10^{10}	1.13	4.14
G58	$BCl + H \rightarrow B + HCl$	2.37×10^{12}	0.47	112.7
	Reverse rate	3.27×10^{10}	1.05	4.76
G59	$BCl_3 + H \rightarrow BHCl_3$	2.33×10^7	-0.54	13.23
G60	$BCl_3 + H \rightarrow BHCl_2 + Cl$	2.31×10^3	1.36	44.8
G61	$BCl_3 + H \rightarrow BCl_2 + HCl$	4.09×10^3	0.97	49.8
G62	$BCl_3 + H \rightarrow BCl_2 + HCl$	2.6×10^4	1.23	108.4

Note: The rate constants are written according to Arrhenius equation: $K = AT^n e^{-E/RT}$. “ $\leftrightarrow$ ” denotes the reverse rates calculated from equilibrium thermochemistry.

2.2 ML

With the great success of data-driven modeling, ML has received increasing attention [31–34]. Considering the production of the variety of intermediate species and the complexity of the deposition process of the CVD- B_xC , we combined a reactor model (RM) with ML, as shown in Fig. 2. Considering N arbitrary samples (X_i, t_i) , where $X_i = [x_{i1}, x_{i2}, \dots, x_{in}]^T \in R^n$, $t_i = [t_{i1}, t_{i2}, \dots, t_{im}]^T \in R^m$. X_i represents the input data set, and t_i is the output data set.

$$X_i = \begin{Bmatrix} x_1(T), x_1(BCl_3), x_1(CH_4), \dots, x_1(BHCl_2) \\ x_2(T), x_2(BCl_3), x_2(CH_4), \dots, x_2(BHCl_2) \\ \dots, \dots, \dots, \dots, \dots \\ x_N(T), x_N(BCl_3), x_N(CH_4), \dots, x_N(BHCl_2) \end{Bmatrix} \quad (16)$$

Error back propagation (BP) algorithm and support vector machine (SVM) are two commonly used machine learning algorithms. They have many applications in material studies [35,36]; thus, they are applied in ML. The BP algorithm is composed of two processes: forward calculation of data stream (forward propagation) and backward propagation of error signal. In forward propagation, the propagation direction is from the input layer to the hidden layer and then to the output layer. The state of each layer of neurons only affects the next layer of neurons. However, if the actual output does not match the expected output, the process of back propagation of errors is then entered. Error back propagation involves passing the output error back to the input layer through the hidden layer, layer by layer,

Fig. 2 ML model design for B/C prediction.

apportioning the error to all units of each layer, and using the error signal obtained from each layer as the basis for adjusting the weight of each unit. Through these two processes alternately, the error function gradient descent strategy is performed in the weight vector space, and a set of weight vectors are dynamically studied to achieve the minimum network error function value. Learning rate and learning error of BP neural network structure are set as 0.01 and 0.001, respectively. Considering the network accuracy and calculation time, three layers of BP neural network structure are selected, and the number of the hidden layer nodes is chosen as 10 by trial-and-error techniques. The N arbitrary samples (X_i, t_i) were entered into the BP neural algorithm program, and the specific steps are as follows:

- 1) Initialize the network, and randomly assign each connection weight and threshold values θ_i, r_i ;
- 2) Compute hidden layers from a given input–output mode pair;
- 3) Calculate new connection weights and thresholds;
- 4) Select the next input mode pair to return to the second step, and repeat the training until the network output error reaches the required training.

The SVM algorithm is very powerful; it not only supports linear and nonlinear classification but also linear and nonlinear regression [37]. In the process of determining the hyperplane with the largest geometric interval, only the sample points closest to the hyperplane play a role. Such sample points are called support vectors. This classification model is also called support vector machine. In practical problems, data is usually not linearly separable in a multidimensional space; that is, in the input space where the data is located, there is no hyperplane that can complete the required classification. A feasible solution is to apply kernel techniques to map data from the input space to a higher dimensional space through a specific function and look for hyperplanes in the higher dimensional space. We call this space a feature space. Because the input space is mapped to a higher dimensional feature space through specific mapping, the amount of calculation in the higher dimensional space will increase significantly, and the computational complexity will also increase significantly.

In the SVM regression, the system attempts to fit as many data as possible into the interval while limiting the margin violation. To reduce the amount of calculation, on the premise that the calculation of the support vector machine involves only the inner product calculation, a kernel function is introduced to convert the inner product

calculation in the feature space into a non-linear transformation of the inner product operation of the data in the input space. SVM needs to adjust the relevant parameters, mainly penalty parameter (denoted as C) and nuclear function parameter (denoted as G), to get a better predictive accuracy. C demonstrates how much the data range could be adapted for data fitting, the greater the C value, the wider the data range, and thus lead to overfitting more likely. G implicitly determines the distribution of the data after mapping to the new feature space. The larger the G , the less the support vector. The number of support vectors affects the speed of training and prediction. With regard to the optimization of C and G , the generally accepted method is to search the optimum values in a certain range. Here C and G are considered as 2.3 and 4 by grid-search techniques, respectively.

It is essential to assess the error during prediction in order to evaluate the performance of BP and SVM models. This could be carried out by comparing the model predicted value and the experimentally measured values. In this regard, mean absolute percentage error (MAPE) and mean square error (MSE) were employed to assess the closeness of prediction values and measured values.

$$\text{MAPE} = \frac{100}{n} \sum_{i=1}^n \frac{|E_i - P_i|}{E_i} \quad (17)$$

$$\text{MSE} = \frac{100}{n} \sum_{i=1}^n (E_i - P_i)^2 \quad (18)$$

where E_i is the measured experimental value, P_i indicates the ML model predicted result, and n refers to the total number of sample points.

3 Results and discussion

3.1 Temperature field distribution

The temperature distribution of the reactor is shown in Fig. 3. The results show that the temperature distribution in the reactor shows a gradient distribution, and the temperature around the deposition substrate is the highest, which is consistent with the actual processing temperature. The temperature distribution in the middle deposition area is relatively uniform (isothermal zone). Due to the size effect of the reactor and the cooling effect of the gas, the temperature gradient near the inlet and outlet of the isothermal zone was relatively large. The precursor was gradually heated and decomposed

Fig. 3 Axial temperature distribution curve in the reactor at different deposition temperatures.

into a large amount of intermediate species when entering the isothermal zone, and then these intermediate species reacted on the substrate surface.

3.2 Distribution of intermediate species

The distribution of the molar fraction of the intermediate species in the reactor is shown in Fig. 4. The concentration of BCl_3 dropped sharply as it approached the substrate, which was consistent with the temperature distribution trend inside the reaction chamber. The main decomposed gas species of BCl_3 in the reaction chamber were BHCl_2 and HCl , and the trends of BHCl_2 and HCl were the same, which was consistent with the main reaction $\text{BCl}_3 + \text{H}_2 \rightarrow \text{BHCl}_2 + \text{HCl}$ [13]. BHCl_2 was considered an intermediate and/or by-product, which were formed by hydrogen reduction of BCl_3 , according to thermodynamic analysis and experimental work [13,38]. Berjonneau *et al.* [13] showed that in the case of a homogeneous reaction, CH_4 still exists in a large amount at high temperatures, and in the case of a heterogeneous reaction, CH_4 will decompose to form boron carbide and graphite as a carbon source. The above situation agrees with our prediction. In addition, we found that some intermediate gas phase components, such as BCl_2 , BCl , BH_2Cl_2 , CHBCl_2 , CHBCl , CH_3 , C_2H_3 , C_2H_5 , and C_2H_6 , have lower molar fractions, indicating that they do not play a dominant role in the B/C ratio of the deposited product during the homogeneous reaction. In addition, Reinisch *et al.* [20] proved that MDB (CH_3BCl_2) was a major intermediate component by FTIR apparatus. Correspondingly, Fig. 4 shows MDB is the third important boron intermediate whose concentration is only lower than BHCl_3 and BHCl_2 . The results obtained from Reinisch *et al.* [20] and our model agrees well with each other.

Fig. 4 Plots of the gas-phase compositions for (a) boron and (b) carbon elements along the reactor height for deposition temperature of 1000 °C, total pressure of 12 kPa, total gas flow rate of 210 sccm, In_{BCl_3} is 2/7, and In_{CH_4} is 1/7.

Figure 5 shows the predicted mole fractions of important species at different temperatures, with a constant feed gas composition and inlet flow rate. The concentrations are the mean values at the substrate surface. Only the major chemical species having a molar fraction larger than 10^{-4} are shown. Low temperature (900 °C) leads to less decomposition of BCl_3 and CH_4 . BHCl_2 has the highest concentration compared to other boron-containing intermediate species. The decomposition of CH_4 is very sensitive to temperature. Remarkably, at 950 °C, the concentration of hydrocarbon increased with temperature, e.g., C_2H_2 and C_2H_4 . The concentration of CH_4 slightly decreased with increasing temperature, and C_2H_4 became the most abundant carbon intermediate. Further, C_2H_2 became the second largest hydrocarbon species at higher temperatures. The shift from CH_4 to C_2H_2 at high temperatures has also been found in hydrocarbon cracking chemistry (C–H system, without B nor Cl). These results demonstrate that the major hydrocarbon species are CH_4 and C_2H_4 , and the major species containing boron are BCl_3 , BHCl_2 , BHCl_3 , and CH_3BCl_2 for a typical CMC processing

Fig. 5 Influence of temperature on the mole fraction of intermediate components: Total pressure of 12 kPa, total gas flow rate of 210 sccm, In_BCl₃ is 2/7, and In_CH₄ is 1/7.

temperature. Our predictions are consistent with Berjonneau's experimental results and thermodynamic calculation [38].

3.3 Predicted boron to carbon ratio

Firstly, BP and SVM were used to directly correlate the deposition atomic ratio with deposition conditions (temperature, input gas ratio, total pressure, reactor inner diameter, and flow rate), without the RM. Figures 6 and 7 show that the functional relationship between them is not very good ($R^2 = 0.938$). The average values of MSE and MAPE are approximately 25% and 30%, respectively.

Next, an RM was established to predict the molar fraction of the intermediate gas species generated in various deposition processes. Then, we used BP and SVM to relate the boron–carbon ratio values of MSE and MAPE were around 6.8% and 8.2%, respectively. Figures 8 and 9 show that the experimental measured

results and predicted values are close to overlapping ($R^2 = 0.975$). As shown in Table 5, after inputting the intermediate gas species predicted by RM into the SVM algorithm, the prediction error was reduced from about 25% to 7%. Compared with the BP algorithm, the prediction of SVM was better. The prediction of SVM was determined by the algorithm itself and affected by the sample size. In the case of small sample data, SVM is recommended.

One important application of the ML approach is to interpolate the correlation of B/C ratio vs. experimental control parameters. Given the fixed processing parameters, we calculate the B/C ratio with temperature in Fig. 10. Our model predicts that the B/C ratio attains a minimum at ~950 °C and then increases to the maximum at 1100 °C. Liu *et al.* [15] found that even at the same gas ratio, the atomic composition obtained at different deposition temperatures is different. Liu *et al.* [15] and we both reach the same conclusion that it is not possible to simply establish a relationship between the gas ratio and the deposition result.

Fig. 6 Goodness of fit (input variables are T , Q , P , In_BCl₃, In_CH₄, and In_H₂).

Fig. 7 Predicted B/C without reactor scale (input variables are T , Q , P , ID , In_BCl₃, In_CH₄, and In_H₂).

Fig. 8 Goodness of fit (input variables are T , P , BCl_3 , CH_4 , BHCl_2 , BHCl_3 , BCl_2 , HCl , and H_2).

Table 5 Mean absolute percentage error and mean square error of predicted results

		SVM (%)	BP (%)	Average value (%)
Without RM	MSE	16.5	34.2	25.35
	MAPE	15.8	45.6	30.7
With RM	MSE	1.7	11.9	6.8
	MAPE	8.4	8.1	8.25

3.4 Sensitivity coefficient analysis

After the training session, sensitivity analysis was performed with SVM. Sensitivity coefficients were calculated with respect to the B/C:

$$S(k) = \frac{v_0 - v}{v} \quad (19)$$

where v_0 is the predicted deposition B/C by SVM training model when the molar fraction of the i -th gas species is fixed as zero, and the concentrations of the other species remain unchanged; v is the original deposition rate predicted by SVM training model.

Therefore, “sensitivity” indicates the degree of influence on the predicted ratio of the components of the deposited product when the studied species is removed. Sensitivity analysis can be used to identify core species in a deposition mechanism. Obviously, a larger $S(k)$ value for a certain substance indicates that it plays a dominant role in the deposition process.

Corresponding to 900, 1000, and 1100 °C, we selected samples 2, 7, and 15 to study S . The sensitivity analysis results (Fig. 11) show that the intermediate species with molar fractions that limit the B/C ratio are BCl_3 , CH_4 , BHCl_2 , BHCl_3 , CH_3BCl_2 , C_2H_4 , C_2H_2 , CH_4 , HCl , and H_2 . The sensitivity coefficients of other species were below 0.01, which suggested they minimally influence the B/C ratio. BHCl_2 and BCl_3 provide the most productivity for boron atoms, while C_2H_4 and CH_4 are the main sources of carbon atoms. The S of CH_4 was the largest, which is consistent with the deposition mechanism proposed by Vandenbulcke [39]. Lartigue *et al.* [40] also indicated that the production of CH_4 is a predominant step toward deposition. The intermediate BHCl_2 was found to be very important to the deposition process, which is also consistent with Vandenbulcke’s experimental results [39].

To compare with the effects of boron- and carbon-containing intermediate species on the composition of deposited products, the S of the main boron- and carbon-containing intermediate species were separately calculated and then compared in Fig. 12. The S of the boron-containing intermediate species increased with temperature. On the contrary, the S values of carbon-containing intermediates were larger at 900 °C, and the values were higher than that of boron-containing species. This is consistent with the reported mechanism, which states that methane decomposes less as compared

Fig. 9 Predicted B/C with reactor scale (input variables are T , P , BCl_3 , CH_4 , BHCl_2 , BHCl_3 , BCl_2 , HCl , and H_2).

Fig. 10 Plots of the B/C ratios with deposition temperature, total pressure is 12 kPa, total gas flow rate is 210 sccm, In_{BCl_3} is 2/7, and In_{CH_4} is 1/7.

Fig. 11 Analysis of the sensitivity of the intermediate species with respect to the B/C under different temperatures by ML.

Fig. 12 Analysis of the sensitivity coefficient of the main intermediate gas species containing boron (B-m) and containing carbon (C-m) at different temperatures.

to boron trichloride at low temperatures. This result is also consistent with the reported thermodynamic calculation results [38]. Therefore, the deposit composition is limited by methane at low temperatures. At 1000 and 1100 °C, the decompositions of the

boron- and carbon-containing intermediate species were similar, which demonstrate a competitive deposition mechanism. Thus co-deposition occurs, and the B/C ratio of the deposits gradually decreased with temperature. We concluded the main factor controlling the boron–carbon ratio is temperature. Methane is the controlling gas species of the deposit compositions at low temperatures (~ 900 °C), while methane and boron trichloride both affect the deposit compositions at higher temperatures (> 900 °C).

4 Conclusions

1) Based on the reported experimental results, we established a simplified two-dimensional reactor model, which couples gas-phase reaction, as well as heat and mass transfer, for a $\text{BCl}_3\text{--CH}_4\text{--H}_2$ system.

2) The main intermediate species were BCl_3 , CH_4 , BHCl_2 , BHCl_3 , CH_3BCl_2 , C_2H_4 , C_2H_2 , CH_4 , HCl , and H_2 , and the changes in BHCl_2 and HCl were the same. This result was consistent with the main reaction $\text{BCl}_3 + \text{H}_2 \rightarrow \text{BHCl}_2 + \text{HCl}$.

3) Comparing ML techniques without RM, the prediction error of ML techniques incorporated with RM reduced from about 25% to 7%.

4) Sensitivity analysis shows that, with the exception of temperature, CH_4 is the key factor in controlling the deposit compositions at low temperatures, while CH_4 and BCl_3 are both important at high temperatures.

In summary, the combination of RM and ML allows for the prediction of the boron–carbon ratio of the deposited product within a reasonable error range (less than 10%). This method can also be applied to other multi-element CVD systems.

Acknowledgements

We thank the National Key R&D Program of China (Grant No. 2017YFB0703200), National Natural Science Foundation of China (Grant Nos. 51702100 and 51972268), and China Postdoctoral Science Foundation (Grant No. 2018M643075) for the financial support.

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