Reaction of CVD BN ceramics in water vapor at 1023–1173 K using different kinetic model

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1. Introduction

Boron nitride (BN) has long been used as a crucible material in inert environments at high temperatures because its structural forms and certain physical characteristics are similar to the properties of different carbon structures.1–6) Recently it has been found that BN can be used as a fiber coating in ceramic-matrix composites.7,8) However, some inherent shortcomings of BN materials must be overcome to attract technological interest. For instance, BN tends to be unstable when exposed to oxygen and water containing atmosphere.2,7–10) A number of researches have been performed on the reaction behavior of BN both experimentally and theoretically under various oxidizing conditions.2,7–13)

Oda et al.10) dealt with the oxidation kinetics of hexagonal BN powder in 8%O2–20%H2O/balance argon at 1173–1373 K. Paralinear weight change curves were observed. A shrinking sphere model was adopted to treat the reaction of BN with the activation energy of 170 kJ/mol or so, indicating the interface reaction of BN and water vapor was the rate-controlling step. Oda and Yoshio11) examined the oxidation of hexagonal BN powder. The reaction followed linear reaction and the shrinkage sphere model was applied. Further investigation indicated that the reaction rate was dependent on crystallographic orientation of BN.

Lavrenco and Alexeev12) compared the oxidation behavior of several types of α-BN (hexagonal structure) and γ-BN (wurtzite structure) plate. The result showed that different kinetic models were applied depending on the structural of BN. The effect of microstructure of BN on the reaction behavior of BN has been further verified in the experiment of Coffer and Economy. In the experiment, a series of BN powder with different interplanar [d(002)] spacings between 3.33 and 3.67Å in water vapor containing atmosphere were investigated. The result showed that the samples with larger interplanar spacings exhibited greater weight loss due to the formation of HBO2. In dry air, the larger interplanar spacings exhibited greater weight gain. In summary, the reaction behavior of BN was affected by various factors including the microstructure of BN, temperature and different oxidizing atmosphere.

Since the reaction of BN in water vapor is a kind of gas-solid reaction, it is very complicated and involved both the oxidation reaction between BN and O2 and the volatilization reaction between B2O3 and H2O. Considering the theoretical investigation is essential to discuss the reaction kinetics and guide the material designing and processing. Various models have been adopted to investigate the reaction kinetics including the shrinking sphere model,10,11) linear rate equation12) and paralinear kinetics13) etc. Among these models, the paralinear kinetics model developed by Tedmon for Cr2O3-forming Fe-C alloys13) has been widely adopted. For instance, Jacobson et al.9) and Opila14) have applied the paralinear kinetics model to deal with the reaction kinetics of BN and SiC in wet oxygen and got a good agreement with the experimental data. However the paralinear kinetics model is not convenient to use because it is an implicit function. In addition, we can only obtain the relationship of the reaction scale thickness or mass change with time. The effect of temperature and water vapor on the reaction behavior cannot be obtained and discussed. Therefore, it is meaningful to get an explicit model in which the reacted fraction can be expressed as a function of temperature, water content and other factors.

Recently Chou et al.15) has developed a new model based on gas-solid reaction, i.e. RPP model (real physical picture), in which it can explicitly express the reacted fraction as a function of time, temperature, sample size as well as many other related physical properties. This formula has been successfully applied to treat the oxidation behavior of carbides and nitrides.16,17) Since the reaction of BN in water containing atmosphere also belongs to gas-solid reaction, it is expected to deal with the reaction kinetics using this new model, aiming to extend RPP model to deal with more gas-solid systems.

In this paper, the reaction behavior of chemically vapor-deposited (CVD) BN ceramics was investigated in wet air.
containing 20 mass% water at 1023–1173 K. Based on this, the reaction kinetics was discussed using RPP model and the paralinear kinetic model used in the literature respectively. A further comparison was also carried out to deal with the reaction behavior of CVD BN in wet oxygen at 1173 K reported by Jacobson et al., expecting to find a more convenient and accurate method to investigate the reaction kinetics of CVD BN ceramics in water-containing atmosphere.

2. Experimental

CVD BN plate was bought from Advanced Ceramics Co. Ltd., Beijing, China. The material was deposited at high temperatures from BCl3 and NH3. The characteristics of BN used in the experiment are listed in Table 1. The main impurities are O, C, Ca and Si. X-ray diffraction (XRD) result for the CVD BN is shown in Fig. 1. It can be seen that the c-axis orientation.

The samples were cut into coupons with dimensions approximately 20 mm × 5 mm × 5 mm with a 2 mm hole for the hangwire. The samples were ultrasonic cleaned with ethanol and dried for experiment. The sample was suspended from a sapphire fiber connected to a recording electrobalance with sensitivity of 0.001 mg. The dry air as the carrier gas was introduced into the quartz tube through a separated entrance and mixed with the water vapor in the quartz tube. The water vapor was generated by a water-vapor generating device composing of a peristaltic pump and heating system. The temperature of the heating system was above 393 K to keep water in the vapor phase. The wet air containing 20 mass% water was flowed downward to prevent condensation of volatile products on the hangwire. When the temperature of the furnace reached to the required temperature, the sample was put into the hot zone of the furnace. The weight change was continuously recorded by the balance linked to a computer for 5 h. To ensure the data to be as accurate as possible, every experiment at the fixed temperature was repeated at least three times and got the average value.

3. Results and discussions

3.1 Reaction behavior

Figure 2 is the TG curves of BN in wet air at 1023 and 1073 K for 5 h. Although variation existed in the experimental data because the weight change was very small during the reaction time, i.e. from 0 to 0.035 mg/cm² (experimental maximum mass change), the weight change obviously increased initially and then decreased with time prolonging. The reaction behavior was related closely to the microstructure of the material. In the experiment, BN was synthesized by the method of chemically vapor-deposition and thus had a highly oriented crystalline structure, i.e. c-axis orientation as indicated in XRD. Therefore the reaction behavior was a mixture of simultaneous parabolic and linear kinetics.

Jacobson et al. also investigated the reaction behavior of CVD BN with density of 2.12–2.19 g/cm³ in wet oxygen. The change was continuously recorded by the balance linked to a computer for 5 h. To ensure the data to be as accurate as possible, every experiment at the fixed temperature was repeated at least three times and got the average value.

| Type of BN deposition, temperature | Density (g/cm³) | Interplanar spacing (nm) | Oxygen (wt%) | Carbon (wt%) | Calcium (wt%) | Silicon (wt%) |
|----------------------------------|----------------|--------------------------|--------------|--------------|---------------|--------------|
| CVD, 1900 K or so               | 2.03           | 0.3486                   | 0.0088       | 0.0048       | 0.002         | 0.11         |

Fig. 1. XRD pattern of CVD BN ceramics used in the experiment.

Fig. 2. A comparison of the reaction behavior between experimental data and theoretical prediction by the paralinear kinetics model for CVD BN in wet air at 1023–1073 K.
ceramics was cut into the dimensions of approximately 3 cm \times 1 \text{cm} \times 1 \text{cm} and then cleaned. The cleaned sample was suspended in the hot zone of the furnace. Wet oxygen with water content of 44–7 ppm was inputted the furnace and the weight change was recorded before and after the reaction for 50 h. Figure 3 shows the typical isothermal reaction curve of CVD BN at 1173 K in wet oxygen for 50 h. The reaction behavior was similar to Fig. 2 and followed paralinear kinetics. It has been reported that the parabolic weight gain was attributed to the following oxidation reactions.

2BN(s) + 3/2O2(g) = B2O3(l) + N2(g) \quad (1)

2BN(s) + 3H2O(g) = B2O3(l) + N2(g) + 3H2(g) \quad (2)

The linear weight loss was due to the formation of HBO2(g) by reaction of water vapor with the B2O3 scale as the following volatilization process. The volatilization species was analyzed by mass spectrometry to be HBO2.

\[
B_2O_3(l) + H_2O(g) = 2HBO_2(g)
\]

3.2 Reaction kinetics

3.2.1 Kinetic models

In view of the reaction kinetics of BN in wet air, there are two typical kinds of models, paralinear kinetics and RPP model.

(1) Paralinear kinetic model

Paralinear oxidation kinetics is a classical model that was deduced in early 1967 by Tedmon for Cr2O3-forming Fe–Cr alloys. This model mathematically described the paralinear oxide scale thickness kinetics with time.\(^{1,3}\) The paralinear kinetics is caused by simultaneous parabolic weight gain and linear weight loss. The parabolic weight gain suggests that some type of diffusion process is the rate limiting. This would be oxygen diffusion inward or chromium diffusion outward.\(^{1,3}\) The linear portion was likely caused by water vapor interactions with the oxide scale to form volatile product. The expression can be described as following by adopting a series of mathematical calculation:

\[
t = \frac{k_p'}{2k_l'} \left[ 1 - \frac{2k_l'x}{k_p'} \ln \left( 1 - \frac{2k_l'x}{k_p'} \right) \right]
\]

where \(t\) is the reaction time, \(x\) is the oxide thickness, \(k_p'\) is the parabolic rate constant for oxidation in unit of thickness/\text{time}, and \(k_l'\) is the linear rate constant for scale volatilization in units of mass/time. At long times, the scale thickness becomes a constant as the oxidation rate equals the volatilization rate. This limiting scale thickness, \(x_l\), is equal to \(k_p'/2k_l'\). Usually the weight changes were measured in the experiment. The above expression can be expressed in terms of measured weight changes by transformation as follows:

\[
t = \frac{\alpha^2 k_p}{2k_l} \left[ 1 - \frac{k_l \Delta w_1}{\alpha k_p} \ln \left( 1 - \frac{k_l \Delta w_1}{\alpha k_p} \right) \right]
\]

\[
\Delta w_2 = -\beta k_l t
\]

\[
\alpha = \frac{\text{MW}_{\text{oxide}}}{\text{MW}_{\text{C}2O} - \text{MW}_{\text{C/N}2}}
\]

\[
\beta = \frac{\text{MW}_{\text{monoxide}}}{\text{MW}_{\text{oxide}}}
\]

where \(\Delta w_1\) is the weight gain due to growth of the oxide scale, \(\Delta w_2\) is the weight loss of the oxide scale due to volatilization, \(k_p\) is the parabolic rate constant for oxidation in units of mass/\text{area}/\text{time}, \(k_l\) is the linear rate constant for oxide volatilization in units of mass/\text{area}/\text{time}. \(MW\) is the molecular weight of the species shown in subscript. The total mass change is the sum of \(\Delta w_1\) and \(\Delta w_2\). At long times when the limiting oxide scale thickness is achieved, the weight change is simply expressed by Eq.(6).

Opila and Ham\(^{14}\) adopted Eqs. (5) and (6) to successfully deal with the reaction of CVD SiC in 50% H2O/50% oxygen between 1473 to 1673 K, which provides sound experimental and theoretical basis for actual aircraft engine combustor conditions. Jacobson et al.\(^{15}\) also employed the paralinear kinetics model to deal with the reaction of CVD BN with high density in wet air at 1173 to 1473 K and got a good agreement with the experimental data. However, the above equations are implicit ones and are not easy to use. The main reason is that the parameters of \(k_p\) and \(k_l\) combine so many variables such as water vapor, the density of sample and gas velocity etc. in them that it cannot offer an explicit expression. Because of the above reasons, the curves obtained from the above equation are very sensitive to the variation of \(k_p\) and \(k_l\) as pointed out by Jacobson et al.\(^{9}\)

![Figure 3. A comparison of the reaction behavior between experimental data and theoretical prediction by the paralinear kinetics model for CVD BN with high density in wet oxygen at 1173 K.](image-url)
(2) RPP model
Chou et al.\textsuperscript{15)} has proposed a real physical picture (RPP) model to deal with the gas-solid reaction under the condition where all kinds of possible controlling steps exist based on the physical principles and mathematical calculation. Compared with the paralinear kinetic model, the biggest character of the RPP model is that it gives an explicit expression of the reacted fraction as a function of time, temperature, gas partial pressure and sample shape etc. To date, the RPP model has been successfully applied to treat the hydrogen absorption/desorption for hydrogen storage materials and the oxidation for ceramics and metal materials.\textsuperscript{16-18)} Since the reaction of BN ceramics in wet air involves the oxidation of BN and the volatilization of B\(_2\)O\(_3\), which belongs to gas-solid reaction, RPP model is expected to deal with the reaction kinetics. In the following section, the RPP model will be deduced. Usually the sample used in the oxidation experiment was in the shape of cubic and suspended in the hot zone of the furnace. According to the RPP model, the reaction experiment was in the shape of cubic and suspended in the hot zone of the furnace. According to the RPP model, the reaction behavior of CVD BN ceramics in wet air will be investigated. Based on this, RPP model and the paralinear formulae, the transformation of variable has to be required prior to using the model.

In view of the reaction kinetics of CVD BN ceramics in the experiment, the value of \(\alpha\) and \(\beta\) for BN can be expressed as following according to Eqs.(7) and (8).

\[
\alpha = \frac{3}{2} \frac{\text{MW}_{\text{BN}}}{\text{MW}_{\text{O}} - \text{MW}_{\text{N}}} = \frac{7}{2}
\]  

\[
\beta = \frac{2\text{MW}_{\text{BN}}}{\text{MW}_{\text{B}} - \text{MW}_{\text{O}}} = \frac{5}{7}
\]

The parameters of \(k_p\) and \(k_l\) can be obtained by solving an implicit equation according to Eqs.(5) and (6). The values at different temperature are listed in Table 2. Jacobson et al.\textsuperscript{9)} also calculated \(k_p\) and \(k_l\) using the paralinear kinetics model for the reaction of CVD BN with high density in wet oxygen at 1173 to 1473 K. The values were in the range of \(4.9 \times 10^{-4} - 4.5 \times 10^{-2}\) mg/cm\(^2\)h, \(k_p\) and \(6.4 \times 10^{-3} - 6.3 \times 10^{-2}\) mg/cm\(^2\)h, which were close to the calculated result in our experiment. Figure 2 was the curves plotted from Eqs.(5) and (6), which fitted well with the experimental data.

In view of the reaction kinetics of CVD BN ceramics at 1173 K in wet air investigated by Jacobson et al.\textsuperscript{9)} the parameters of \(k_p\) and \(k_l\) can be obtained by solving an implicit equation to be \(4.2 \times 10^{-4}\) mg/cm\(^2\)h and \(6.0 \times 10^{-3}\) mg/cm\(^2\)h, which were consistent with the resulted reported in literature.\textsuperscript{9)} As shown in Fig. 3, the curves obtained from the paralinear kinetics model fitted the experimental data with good accuracy. Because the gasification temperature of B\(_2\)O\(_3\), 1773 K, was much higher than the experimental temperature, the evaporation of B\(_2\)O\(_3\) during the experiment can be omitted.

### 3.2.3 Application of RPP model
Here RPP model, Eqs.(9) and (11) are combined to describe the reaction behavior of CVD BN ceramics in wet air. There are two parameters, i.e. \(t_{p1}\) and \(t_{p2}\) required to be fitted from the experimental data. By nonlinear regression of the experimental data, \(t_{p1}\) and \(t_{p2}\) were extracted to be 3.16 \(\times 10^8\) and 1.82 \(\times 10^7\) at 1023 K. The values were calculated to be 2.56 \(\times 10^8\) and 1.09 \(\times 10^7\) at 1073 K. Based on the above formulae, the theoretical reaction curves for BN ceramics were plotted in Fig. 4 for comparison. A fairly agreement has been obtained between the experimental data and the calculated lines, verifying the RPP model is reasonable. In view of the expression of \(t_{p1}\) and \(t_{p2}\) [Eqs.(10) and (12)], the apparent activation energy \(\Delta E_p\) and \(\Delta E_f\) can be further extracted to be 105.8 and 93.5 kJ/mol.

In an analogous way, \(t_{q1}\) and \(t_{q2}\) for the reaction of CVD BN in wet air investigated by Jacobson et al. were extracted to be 2.73 \(\times 10^8\) and 62.7 using RPP model. Based on the above formulae, the theoretical reaction curve for monolithic BN ceramics is also plotted in Fig. 5 for comparison. A fairly agreement was obtained between the experimental data and the calculated line, verifying the RPP model was reasonable.

### 3.3 Comparison of the two models
From the above application and comparison of the two models, the major difference between PRR model and the paralinear kinetic model is that, PRR model describes explicitly the weight change as a function of temperature \(T\), diffusion coefficient

### Table 2. \(k_p\) and \(k_l\) values obtained from the paralinear kinetics model

| CVD BN     | \(k_p\) (mg/cm\(^2\)h) | \(k_l\) (mg/cm\(^2\)h) |
|------------|------------------------|------------------------|
| 1023 K     | \(1.9 \times 10^{-4}\)  | \(9.6 \times 10^{-3}\)  |
| 1073 K     | \(1.8 \times 10^{-4}\)  | \(9.8 \times 10^{-3}\)  |
Do, sample shape, gas partial pressure $P_{\text{eq}}$ gas and reaction time $t$ etc. This makes it very convenient to carry out a theoretical discussion. This advantage has been proved in our recent work in dealing with the oxidation reaction of nonoxide materials. It is well known that the activation energy, $\Delta E$, is a very useful parameter to evaluate the stability of material. It can be obtained from both the two models. However, we can directly obtain the value when using the RPP model because it is an explicit expression by nonlinear regression method just one time. By contrast, it needs many times of regression to get the value when adopting the paralinear kinetic model. This will possibly cause larger errors. The calculation error from the two models can be obtained by using the following equation:

$$\Delta = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{(x_i)_{\text{mea}} - (x_i)_{\text{cal}}}{(x_i)_{\text{mea}}} \right| \times 100\% \quad (15)$$

where $\Delta$ is average relative error, $(x_i)_{\text{mea}}$ is experimental data measured, $(x_i)_{\text{cal}}$ is the value calculated from the model and $N$ is the sum of experimental points. According to Eq.(15), the errors for the reaction of CVD BN calculated from the paralinear kinetics and RPP model are listed in Table 3. It can be seen that the error calculated from the RPP model is smaller than that from paralinear kinetics. To further validating the performance of RPP model, the reaction behavior of hexagonal BN powder exposed to wet air (containing 6.5 mass % H$_2$O) at 1173–1373 K for 18 h was carried out in our recent work. The reaction kinetics was adopted using RPP model and the paralinear kinetics respectively with the relative errors to be 6.86 and 15.7%, indicating RPP model is prefer. Actually, the above analysis will be not limited in the treatment of reaction of BN ceramics, but should be suitable for all kinetic problem of gas-solid reaction. However, they must be the kinetic
Table 3. Comparison of the calculation error from the paralinear kinetics model and RPP model

|                      | Calculated from the paralinear kinetics model | Calculated from RPP model |
|----------------------|-----------------------------------------------|----------------------------|
| CVD BN reported in the literature9) | 6.4%                                         | 4.8%                       |
| CVD BN               | 16.5%                                        | 11.3%                      |

The paralinear kinetic model is a very popular one currently being used to treat the kinetics of nonoxide ceramics at the atmosphere containing water vapor. However it is not a good choice because it is an implicit function and could not meet the real physical picture for most of practical cases. In addition, it will lead to a large error accumulation due to the poor chemical reaction took place predominantly and the two models were not applicable. As to the situations where the rate-controlling step is located in the step other than a diffusion controlled, the similar formulae could also be derived and the advantages of our treatment mentioned above should be kept.

4. Conclusions

The paralinear kinetic model is a very popular one currently being used to treat the kinetics of nonoxide ceramics at the atmosphere containing water vapor. However it is not a good choice because it is an implicit function and could not meet the real physical picture for most of practical cases. In addition, it will lead to a large error accumulation due to the poor mathematical treatment. By comparison, RPP model gives an explicit expression that makes us possible to extract the useful physical property in one time regression. As a result a more accurate value could be obtained. Therefore the reaction behavior can be predicted within the same reaction mechanism, which is very important for high-temperature ceramics application.

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Nomenclature

- $k_p$ the parabolic rate constant for oxidation in unit of thickness² per unit time
- $k_l$ the linear rate constant for scale volatilization in units of thickness/time
- $k_p$ the parabolic rate constant for oxidation in units of mass²/area*time
- $k_l$ the linear rate constant for oxide volatilization in units of mass/area time
- $x$ the oxide thickness
- $\Delta w_1$ the weight gain due to growth of the oxide scale
- $\Delta w_2$ the weight loss of the oxide scale due to volatilization
- $L_0$ the depth of the sample in units of mm
- $M_0$ the width of the sample in units of mm
- $H_0$ the height of the sample in units of mm
- $D_{p0}$ a constant independent of temperature
- $k_0$ a constant depending on the temperature
- $\nu_m$ a coefficient related to the density of reactant and product
- $P_{gas}$ partial pressure of gas in gas phase
- $\Delta E_d$ the activation energy of the reaction diffusion controlled
- $\Delta E_r$ the activation energy of the reaction chemical reaction controlled
- $R$ gas constant
- $t$ time in hour
- $T$ absolute temperature with K

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