Effect of water-vapor content on reaction rate of hexagonal BN powder at 1273K

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Abstract: Hexagonal BN powder with average particle size of 1.2μm was exposed at 1273K in H_2O/air gas mixture with the range of mass ratio from 0:100 to 6.5:100 at a total pressure of 1 atm. Thermalgravimetry(TG) method was used to measure the reaction behavior of BN powder in water vapor. XRD and SEM were employed to analyze the phases and morphological revolution during reaction. The TG curves showed that the overall reaction process could be divided into two stages. In first stage, weight gained rapidly and the main reaction was the oxidation of BN. The weight gain turning point of the curves with different water-vapor contents varied, indicating that water-vapor had an impact on oxidation rate to some degree. In second stage, weight loss due to B_2O_3 reacting with H_2O to form volatile product. The rate of weight loss increased with increasing the water vapor content. The reaction rate was described by a linear rate law, i.e., $\alpha = - k_l t$. The relationship between k_l and partial pressure of water vapor p was described by a function of $k_l = 0.4p$. The determination of the activation energy was complicated due to variations in the reaction mechanism.

Keywords: Reaction kinetics, water-vapor, content, BN, powder

1. Introduction

Hexagonal boron nitride (*h*-BN) is used as crucible material and solid lubricant on account of its excellent chemical resistance and thermal stability. Recently it has found that BN as a fiber coating in ceramic matrix compounds could prolong the service life of the materials [1, 2]. However, for these applications, BN is often to be exposed to high temperature and water vapor atmosphere. It is found the oxidation of BN was sensitive to even small amounts of water vapor.[3] So it is important to investigate the reaction behavior and the related mechanism of BN recession in water vapor.

Many studies have been done on BN oxidation [4-10], which show the oxidation behavior is complex with the volatilization of B_2O_3. K. Oda et al.[4] have given the primary oxidation reaction of BN, which is

$$BN(s) + \frac{3}{4}O_2(g) = \frac{1}{2}B_2O_3(l) + N_2(g) \qquad (1)$$

This reaction is generally accepted by researchers. Compared to the researches on oxidation of BN, little information is available in the literature concerning the reaction between BN and H_2O, which is of industrial importance. Several studies considered water vapor as a factor to the reaction, [6, 11, 12] but there was no systematic research. T. Matsuda has examined the effects on CVD-BN in different temperature and pressure, it was found that CVD-BN had a high moisture resistance at lower pressures above 1673K; while at higher pressures and below 1673K, it showed poor moisture resistance.[6] N. Jacobson et al.[3] investigated the reactions of three types of BN specimens under water vapor conditions, i.e., hot-pressed BN (HP-BN), high-density CVD BN and low-density CVD BN. There was about 10-20ppm water vapor introduced into the gas steam of high-density CVD BN. Linear kinetics were observed in both reactions of HP-BN and low-density CVD BN, while for high-density CVD BN, the kinetics appeared paralinear behavior because of the present of water vapor increased reaction rate by created volatile HBO_2. A. N. Streletskiiet et al.[12] studied the reaction between BN and water. It was found that BN was isolate in water and did not interact with H_2O molecules, except for the mechanical activation of BN which promoted its interaction with water. Generally, reported reaction kinetics for BN in literatures varies widely, they focused on inconsistent research perspectives. Furthermore, all of the results showed that water vapor played an important role in the reaction process. However the reaction mechanism is not clear.

In this work, different water-vapor contents would be used to investigate the effects of water vapor on both macro and micro structure of BN. The reaction curves will be obtained using TG. The microstructures were determined by SEM, and the phases after reaction were confirmed by XRD.

2. Experimental

The material that was used in this study was commercial hexagonal boron nitride powder with average particle size of 1.2 μm. BN powder of about 1000 mg was homogenously spread out in an alumina crucible and the depth of the powder was about 2mm.

The schematic reaction equipment is shown in Figure1. This apparatus was intentionally designed to apply situ measurement technology. The key part of the equipment is the water vapor generating device which is composed of a peristaltic pump and heating system. Deionized water was supplied into the furnace through the device. The temperature marked in the scheme was kept above 393K by hotline to make sure the liquid water turned into vapor phase. The carrier gas was introduced into the quartz tube through a separated entrance and mixed with water vapor there. Because the volume of water vapor and air are sensitive to temperature, the ratio of water vapor to air was adopted by mass ratio. The mass ratio of liquid water to air at room temperature and standard states was listed in Table 1. When the temperature of the furnace reached to the required temperature, i.e. 1273 K, the sample was put into the furnace. The weight change will be continuously recorded by the mass balance with sensitivity of 0.001g for 18 hours. After reaction, the phase composition and morphology were determined by XRD and SEM.

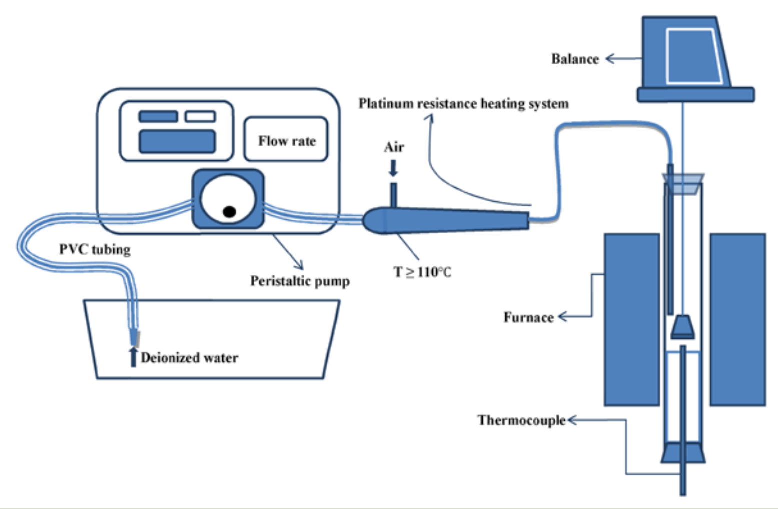

Fig. 1 The Schematic of reaction equipment

Table 1 The ratio of H_2O to air at room temperature

H_2O(l)/air volume ratio	H_2O/air mass ratio
0:100	0:100
0.002:100	1.5:100
0.005:100	3.5:100
0.007:100	5.0:100
0.009:100	6.5:100

3. Results and Discussion

3.1 Thermodynamic calculation

When boron nitride powder was exposed in combustion environment, the possible reaction between combustion gases and boron nitride are listed as follows:

$$BN(s)+\frac{3}{4}O_2(g)=\frac{1}{2}B_2O_3(l)+N_2(g) \qquad (1)$$

$$BN(s)+\frac{5}{4}O_2(g)=\frac{1}{2}B_2O_3(l)+NO(g) \qquad (2)$$

$$BN(s)+\frac{7}{4}O_2(g)=\frac{1}{2}B_2O_3(l)+NO_2(g) \qquad (3)$$

$$BN(s)+\frac{3}{2}H_2O(g)=\frac{1}{2}B_2O_3(l)+\frac{1}{2}N_2(g)+\frac{3}{2}H_2(g) \qquad (4)$$

$$BN(s)+H_2O(g)=\frac{1}{2}B_2O_3(l)+\frac{1}{2}NH_3(g) \qquad (5)$$

$$\frac{1}{2}B_2O_3(s)+\frac{1}{2}H_2O(g)=HBO_2(g) \qquad (6)$$

$$\frac{1}{2}B_2O_3(s)+\frac{1}{2}H_2O(g)=\frac{1}{6}(HBO_2)_3(g) \qquad (7)$$

$$\frac{1}{2}B_2O_3(s)+\frac{3}{2}H_2O(g)=H_2BO_2(g)+\frac{1}{4}O_2(g) \qquad (8)$$

$$\frac{1}{2}B_2O_3(s)+\frac{3}{2}H_2O(g)=H_3BO_3(g) \qquad (9)$$

The reaction Gibbs energy has been calculated using thermodynamic computer modeling package FactSage [13]. The function of the reaction Gibbs energy with temperature for the reactions (1-9) is shown in Figure 2. The partial pressures of the products and those of O_2, water vapor are listed in Table 2. The activity of B_2O_3 (*l*) was assumed to be 1 for all reactions.

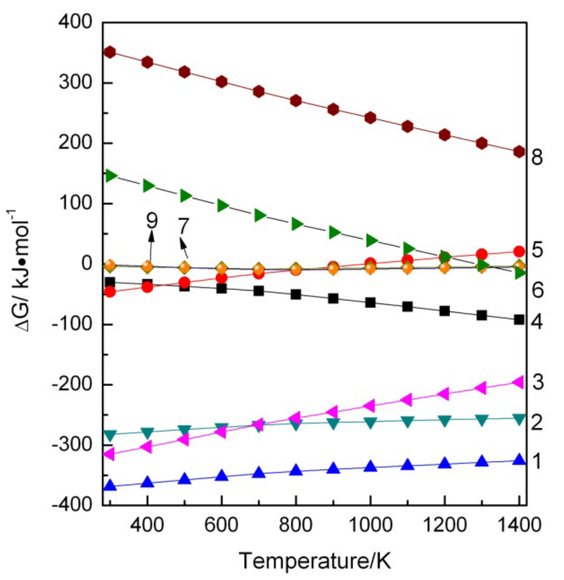

Fig.2 The reaction Gibbs energy of the possible reactions between BN in combustion environments

Table.2 partial pressures of the reactions and products

gases	N_2	NO	NO_2	H2	NH_3	HBO_2	H_2BO_2	H_3BO_3	$(HBO_2)_3$	O_2	H_2O
Partial pressure /MPa	0.055	0.024			0.012	1.5×10^{-4}			5×10^{-5}	0.015	0.03

Among these reactions, it can be seen that the reaction Gibbs energy of Eq. (8) is positive, meaning this reaction could not occur from thermodynamic viewpoint. The other reactions can occur in the temperature investigated since the reaction Gibbs energies are negative. By comparison, the reaction of BN with O_2, i.e., Eq. (1) shows the most favorable tendency to occur even at lower temperatures. Even though water vapor could also react with BN directly according to Eq. (4), however the value of the Gibbs energy of Eq.(1) is more negative than that of Eq.(4), indicating that Eq.(1) is preferred in the temperature range investigated.

From above thermodynamic calculations, the reactions of BN in water-vapor can be divided into two stages: (1) BN reacts firstly with O_2 to form B_2O_3; and (2) B_2O_3 reacts with H_2O.

3.2 Effect of water vapor content on reaction

Typical TG curves of the reaction of BN powder with different water vapor contents at 1273K is shown in Figure 3. For comparison, the reaction of BN with dry air was also carried out and the result was shown as curve 1. Curves 2 to 5 represented the reactions of BN with different water vapor/air mass ratios. The reaction fraction is given as: $\alpha=\Delta W/W_0$, where ΔW means the weight change observed at time t and W_0 is the original weight of *h*-BN powder. From Fig.3, there appears that the reaction of BN with water vapor consisted of two stages: rapid weight gain stage and slower weight loss stage. In the first stage, there seems that all the reactions have the same average reaction rate while the weight gain turning points are different, reflecting some influence of water vapor on reaction. However the reaction of BN with O_2 is still the main reaction. In the second stage, weight loss occurred and the rate increased with the water vapor content increasing. According to the report in the literature, the weight loss was caused by the reaction of B_2O_3 with water vapor to form volatile product HBO_2 [14].

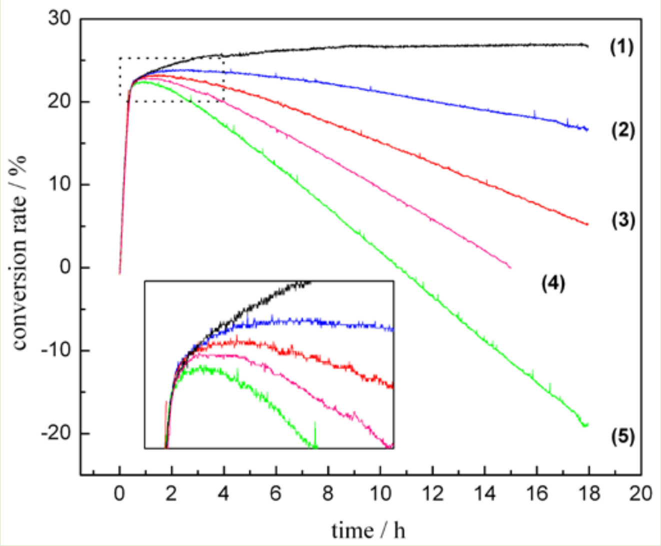

Fig.3 Reaction curves of BN powder with different H_2O/air mass ratio at 1273K for 18h: (1) 0:100; (2) 1.5:100; (3) 3.5:100; (4) 5:100; (5) 6.5:100.

Linear kinetics are observed in the second period which can be described as follows, $\alpha = - k_l t$. where t is the time, and k_l is the linear rate constant in h^{-1} for the volatilization reaction (1). The relationship can be expressed as an equation: $k_l = 0.4p$. where p stands for partial pressure of water vapor.

The value of α should be 40% if *h*-BN powders are completely oxidized. While in the experiment, the total α of the samples was calculated to be no more than 24%. That can be explained by the protective coating produced on BN powder surface. When the oxidation reaches a certain level, a thin transparent liquid B_2O_3 film has formed which inhibits the reaction to further occur and the rate of weight gain therefore slows down. This is consistent with the observation of boron carbon, silicon nitride and titanium carbide [15-17].

3.3 Phase composition and microstructure

XRD analysis of BN powders reacted with various water vapor contents for 18 hours at 1273K were carried out. The XRD patterns are shown in Figure 4. In the experiment, it was found that the samples and the alumina crucible had been stuck together and hard to separate. Therefore the phase of Al_2O_3 also appeared as shown in Figure4. The relative intensity of B_2O_3 phase decreases with the water vapor content increasing, indicating the reaction of B_2O_3 with H_2O occurred more quickly with higher water vapor content.

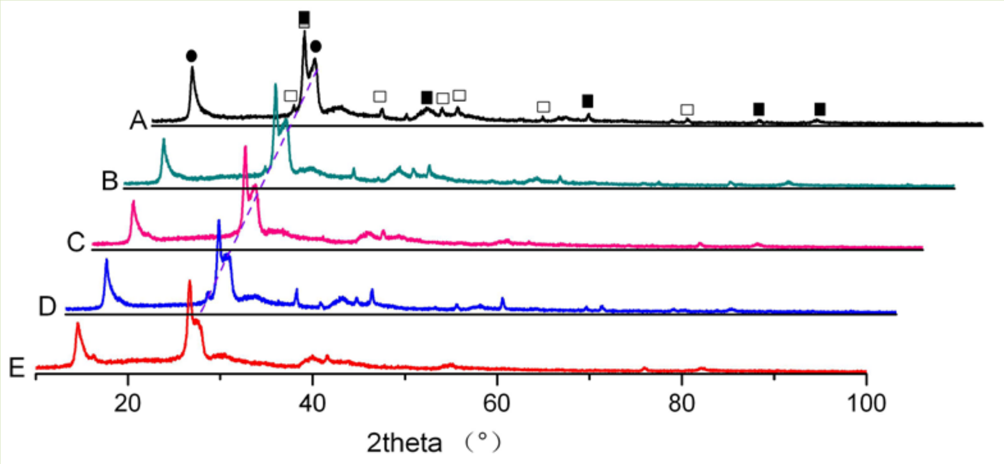

Fig. 4 XRD patterns of BN powder reacted with different H_2O/air mass ratio at 1273K for 18h (A) 1.5:100; (B) 3.5:100; (C) 5:100; (D) 6.5:100. (O) BN powder before reaction. (●)B_2O_3, (■)BN, (☐) Al_2O_3.

Figure **5** shows the SEM images of *h*-BN after the reaction. B_2O_3 was found in all the surface of the samples, which is consistent with the XRD results.

The cross section of *h*-BN powder after reaction is showed in Figure 6. The bulk particles stand for *h*-BN and the gaps for B_2O_3. It can be observed that *h*-BN particles became larger and were surrounded by the phase of B_2O_3. It can be assumed that at the initial stage of the reaction, BN powders first get together and become into blocks as the temperature increases. When the reaction occurs, the surface of BN powder was encompassed by B_2O_3. Since B_2O_3 easily becomes liquid phase at higher temperature, it lead to the phase of B_2O_3 connect with each other. At longer time interval, the reaction of B_2O_3 with H_2O domains and cause the structure of B_2O_3 porous as shown in Figure 6.

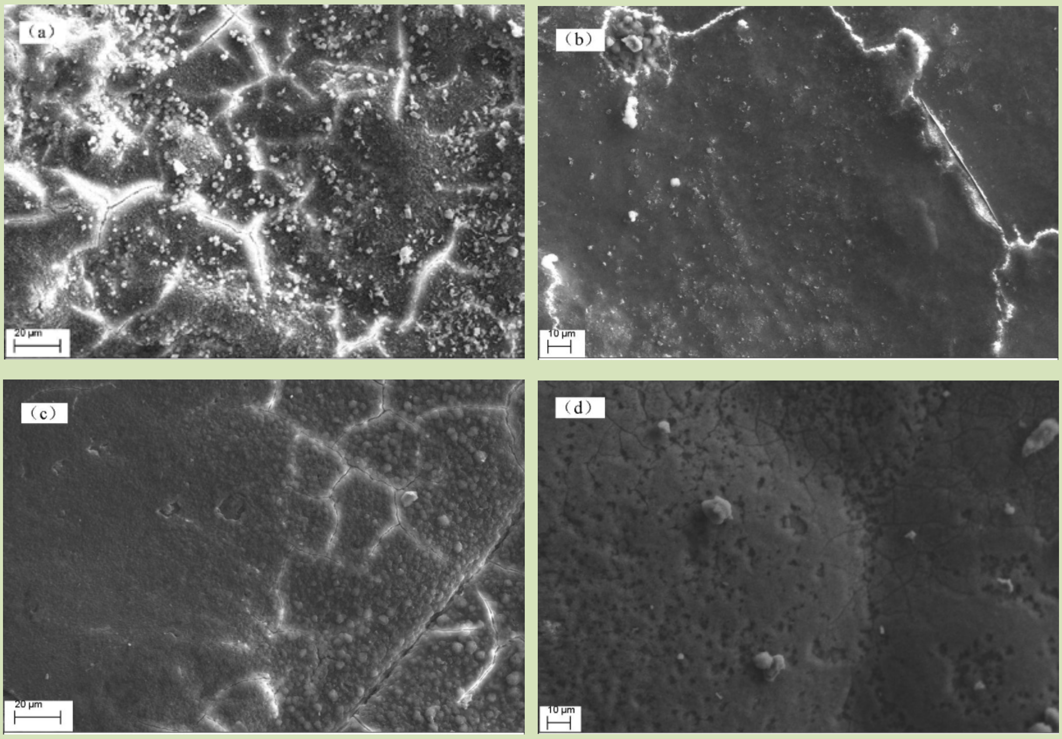

Fig.5 SEM of the surface of *h*-BN under different H_2O/air mass ratio conditions at 1273K for 18h (a) 1.5:100; (b) 3.5:100; (c) 5:100; (d) 6.5:100.

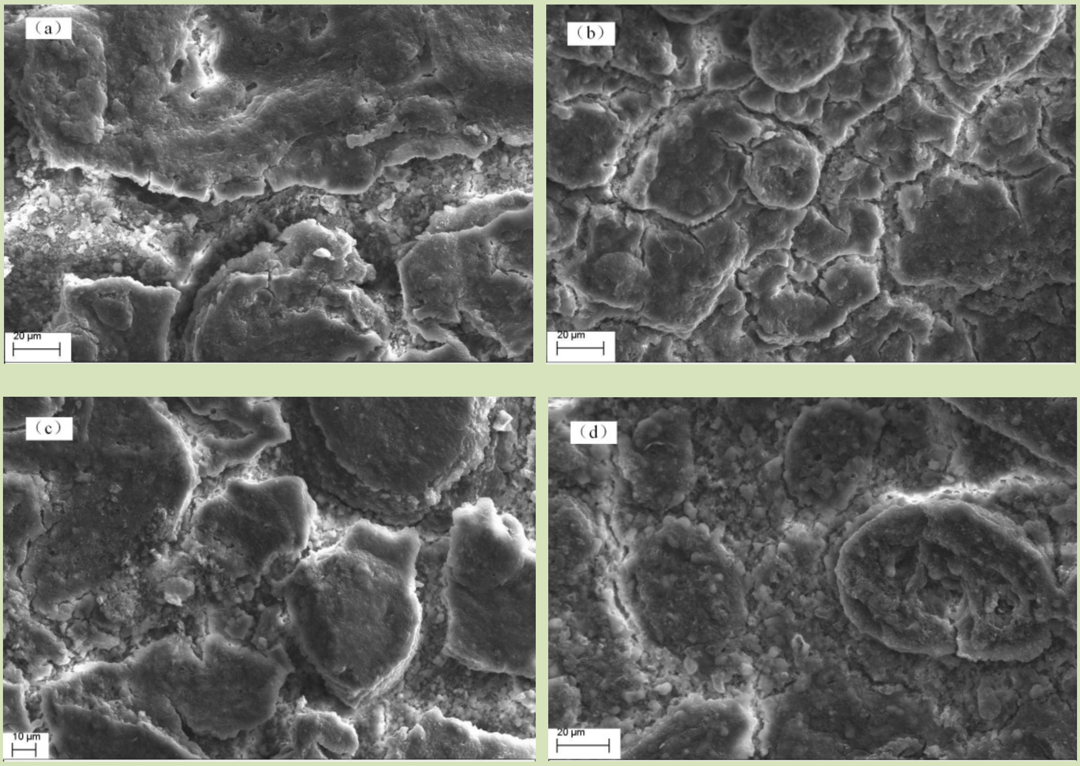

Fig.6 SEM of the cross sections of the h-BN under different H_2O/air mass ratio conditions (a) 1.5:100; (b) 3.5:100; (c) 5:100; (d) 6.5:100.

3.4 Reaction mechanism

According to the above results, the reaction mechanism of BN powder under water vapor conditions can be described in Figure 7. When *h*-BN powder was exposed in high temperature, they would be sintered and the particles became larger. When the reaction began, the surface of BN block was oxidized into liquid B_2O_3 particles, which grew gradually and became large enough to connect with each other. Since the liquid layer of B_2O_3 at the surface of BN powder prevented O_2 from reacting with BN directly, the reaction rate slowed down (as shown in curve 1 of Figure 3). At the same time, the reaction of B_2O_3 with H_2O occurred. As the reaction proceeded, the volatile products make the surface be porous, which provided a path for O_2 to reach the BN/B_2O_3 interface and make the oxidation further occur. Generally, the reaction becomes complicated because the oxidation product B_2O_3 tended to become liquid phase at high temperature, which led to the reaction to belong to a three-phase reaction, i.e. gas-liquid-solid reaction. Further systematic work is still required to reveal the reaction mechanism of BN under water vapor conditions.

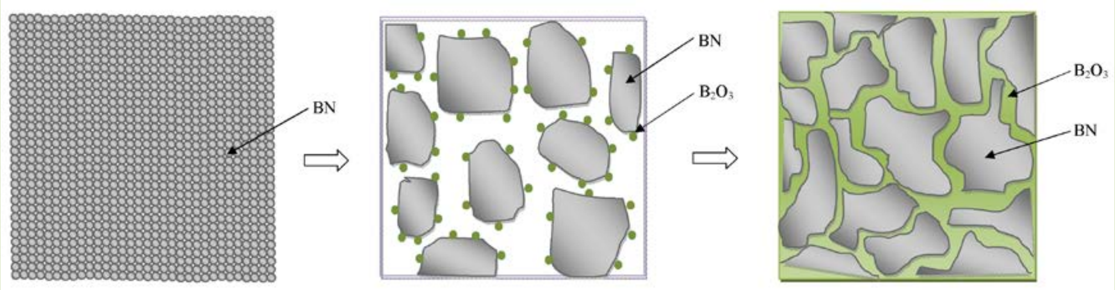

Fig. 7 Schematic diagram of the reaction process of *h*-BN powder with water/air

4. Conclusions

(1) The reaction behavior of *h*-BN powder in combustion atmosphere has been calculated from the thermodynamic point. The results show that the reactions of BN in water-vapor can be divided into two stages: (1) BN reacts firstly with O_2 to form B_2O_3; and (2) B_2O_3 reacts with H_2O.

(2) From the TG experiments, the reaction of BN with water vapor consisted of two stages: rapid weight gain stage and slower weight loss stage. In the first stage, the reaction of BN with O_2 is the main reaction and the product is B_2O_3. At high temperature, a thin transparent liquid B_2O_3 film has formed which inhibits the reaction to further occur and the rate of weight gain therefore slows down. In the second stage, weight loss occurred because of the reaction of B_2O_3 with water vapor to form volatile product.

(3) The kinetics shows that the reaction rate between water vapor and B_2O_3 follows a linear rate law, i.e., $\alpha = -k_l t$. And the relationship between k_l and partial pressure of water vapor p was described by a function of $k_l = 0.4p$.

Acknowledgement

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