Oxidation of BN-ZCM Composite Ceramics

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ABSTRACT

The present paper investigates the oxidation kinetics of BN-ZCM composite ceramics in the temperature range of 1473K-1773K. Oxidation experiments with powder and plates of BN-ZCM composite ceramics have been carried out in air. Oxidation kinetics, products and structures of BN-ZCM have been examined and discussed. The overall activation energy of chemical reaction is 254 kJ / mole and the overall activation energy of diffusion is 289 kJ / mole.

1. INTRODUCTION

With excellent resistance to thermal shock and chemical corrosion, BN-oxides composite refractory is an ideal engineering ceramics and advanced refractory /1-3/. But BN composite refractory will be oxidized at high temperatures, which may limit its application in many aspects. Therefore, its resistance to oxidation is an important property. Though a few papers /4-6/ have been published on the oxidation of BN or its composite refractory, the mechanism of its oxidation has not been understood and the evaporation of B_2O_3, an oxidation product, has not been considered.

This paper will investigate the oxidation behavior and kinetics of BN-ZCM, composite ceramics, where ZCM represents a mixture (or composite) of zirconia (ZrO_2), corundum (Al_2O_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$). Oxidation experiments have been carried out with both powder and plates of BN-ZCM in the temperature range of 1373-1573K. The oxidation kinetic parameters of BN-ZCM composite ceramics have been estimated and discussed.

2. EXPERIMENTAL

2.1 Materials

BN, ZrO_2, Al_2O_3 and $3Al_2O_3 \cdot 2SiO_2$ were used as the starting materials to synthesize BN-ZCM composite ceramics. These starting materials, which are all analytically pure, were provided by Fangda Scientific Ceramics Company of Tsinghua University.

BN-ZCM composite ceramics were prepared by hot-pressing sinter in nitrogen gas flow. They have the composition of 50mass%BN, 15%ZrO_2, 26%Al_2O_3 and 9% ($3Al_2O_3 2SiO_2$).

The argon gas (<5ppm O_2) used in the experiment was purified by passing through columns of silica gel and dehydrate $Mg(ClO_4)_2$ to remove moisture, through ascarite to remove carbon dioxide, and through tube furnaces containing copper and magnesium at 773K to remove residual oxygen.

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2.2 Experimental procedures and results

The oxidation of BN-ZCM was carried out on a SETARAM TGA92 (SETARAM; Calure cedex, France BP34-69641) system. Carefully weighed amounts of both powder and plate samples were held in suitable platinum containers and suspended in the transducers.

In non-isothermal experiments, air was let into the reaction tube after the sample was introduced into the furnace. Then it was heated from room temperature to the temperature of 1773K at fixed heating rates. The results are shown in Fig.1.

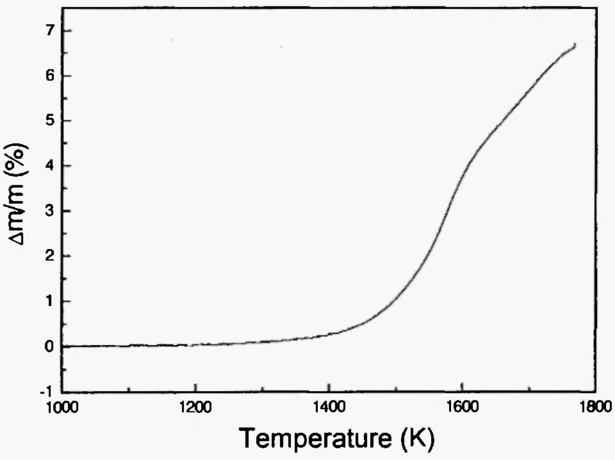


Fig. 1: Oxidation curves of BN-ZCM as temperature increases

In the case of isothermal experiments, the reaction tube was initially evacuated for 15 minutes and then flushed with purified argon gas. The furnace was then heated at a fixed rate (25°C/min.) to the required temperature. After maintaining the required temperature for 5 minutes, air was led into the reaction tube at a flow of about 800 ml/min (preliminary experiments show that gas flow higher than 600 ml/min is above the starvation rate) to replace the argon. At the end of the experimental run, the reaction was arrested by replacing the air flow by argon and the furnace was allowed to cool at the rate of 99°C/min to room temperature. The results are shown in Fig. 2 and Fig. 3.

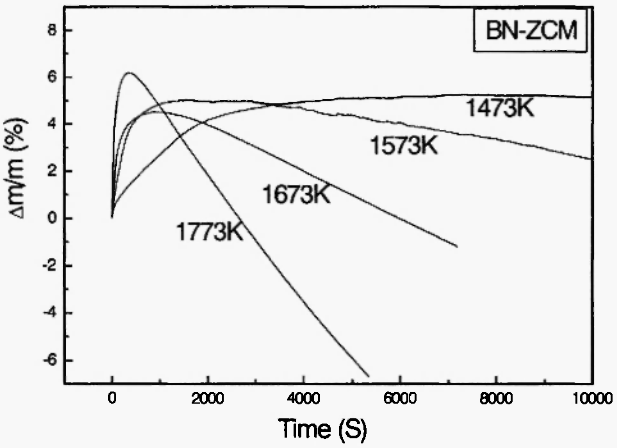


Fig. 2: Isothermal oxidation of BN-ZCM powder

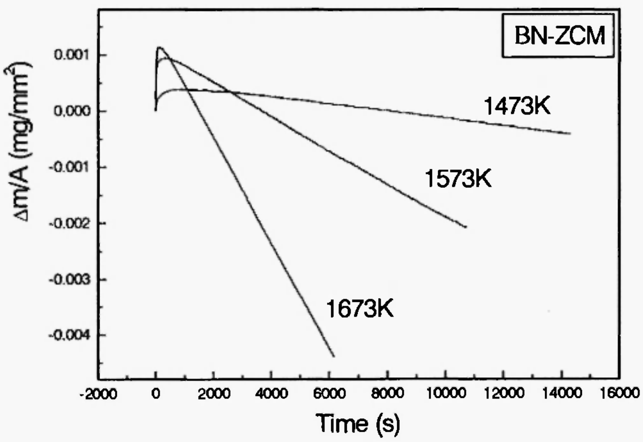


Fig. 3: Isothermal oxidation of BN-ZCM plates

3. DISCUSSION

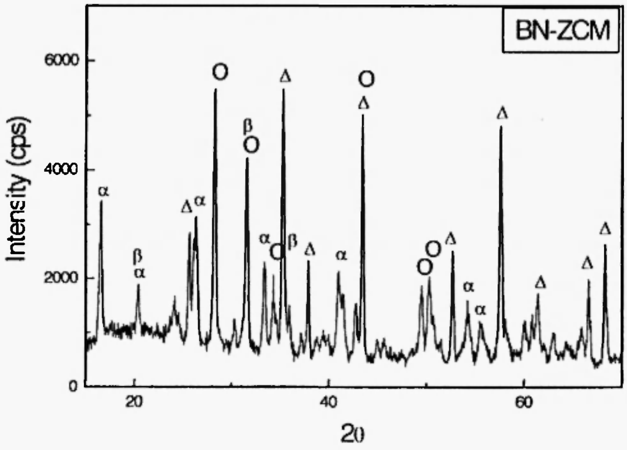
The oxidation reaction of BN-ZCM may be represented by reaction (1) as:

$$\text{BN-ZCM} + O_2 \rightarrow B_2O_3 + \text{ZCM} + N_2 \quad (1)$$

The oxidation of BN-ZCM is a complicated process. At high temperatures, BN will be oxidized into B_2O_3. Simultaneously, B_2O_3 will evaporate into air because of its high equilibrium pressure.

X-ray diffraction analysis was introduced to determine the oxidation products by X-ray diffractometer with Mo K_α radiation (D/max-1200). The results are shown in Fig. 4.

As can be seen in Fig. 4, though B_2O_3 is produced during oxidation process, the main crystal phases are Al_2O_3 and ZrO_2 due to the evaporation of B_2O_2.



Δ-α-Al_2O_3, O-ZrO_2, α-A_9B_2, β-SiO_2

Fig. 4: Oxidation products of BN-ZCM

After the oxidation, BN-ZCM plates were analysed by AFM (atomic force microscope). The results are shown in Fig.5. As oxidation temperature increased from 1473 to 1673K, the roughness degree of the surface increases greatly from 63 to 406μm because of the evaporation of B_2O_3. The degree of roughness is calculated by the following equation:

$$R = \left[N^{-1}\sum(Z_i - Z_{av})^2\right]^{1/2} \tag{2}$$

where R is the degree of roughness, N the number of points, Z_i the height of point i, Z_{av} the average height of all points.

During the oxidation process, as BN oxidizes into B_2O_3, the specimen will have a weight gain. On the other hand, as B_2O_3 evaporates into air, the specimen has a weight loss. For the oxidation of BN-ZCM plates, the rate of evaporation of B_2O_3 can reasonably be assumed to be constant. Suppose that the volume of plate remains almost the same during the process. The weight gain during the oxidation of BN-ZCM plate is

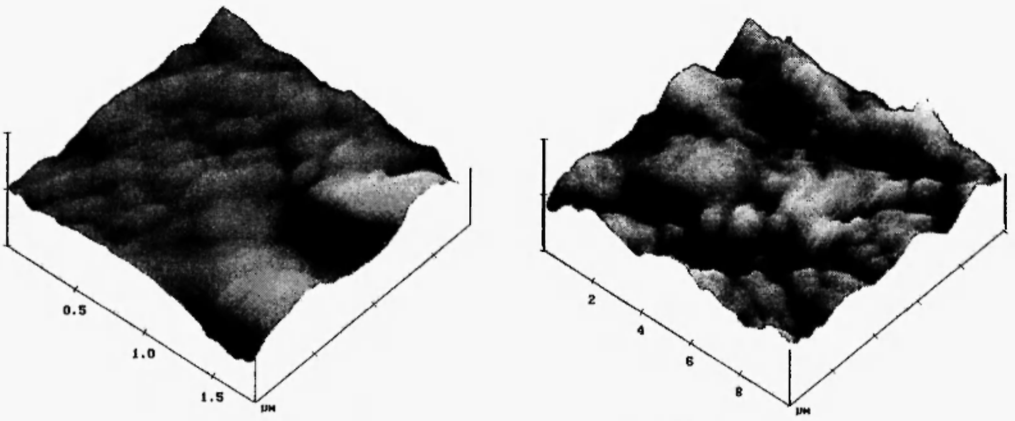
$$\frac{d(\Delta w_0)}{dt} = A_0(\theta'\rho_{B_2O_3} - \theta\rho_{BN})\frac{dx}{dt} \tag{3}$$

where: Δw_o is the weight gain of oxidation process (not considering the evaporation of B_2O_3), A_0 the surface area of the sample, θ and θ' the volume content of B_2O_3 and BN respectively, x the thickness of oxidation layer, ρ_{B2O3} and ρ_{BN} the density of B_2O_3 and BN respectively,

For the evaporation of B_2O_3, the weight loss can be expressed as

$$\frac{\Delta w_e}{A_0} = \frac{\theta' A_0 x_2 \rho_{B_2O_3}}{A_0} = k_e t \tag{4}$$

where Δw_e is the weight loss of B_2O_3 evaporation during the oxidation process, x_2 the thickness of the



(a:1473K)

(b:1673K)

Fig. 5: AFM Photos of BN-ZCM

evaporated layer, k_e is the rate constant of B_2O_3 evaporation.

Initially, oxidation occurs at the surface of BN-ZCM (or the product layer is very thin), chemical reaction is the rate-controlling step. Then

$$r_o = \frac{d(\Delta w_o)}{dt} = A_0 k_r C \qquad (5)$$

where, k_r is the rate constant of chemical reaction and C is the content of oxygen at surface. Integration of equation (5) yields

$$\frac{\Delta w_o}{A_0} = k_r Ct = k_o t \qquad (6)$$

where $k_O=Ck_r$, as C is constant, then k_O, the rate constant of oxidation process, is also constant. Consider weight loss by B_2O_3 evaporation and let w express the total weight change, then

$$\frac{\Delta w}{A_0} = \frac{\Delta w_o - \Delta w_e}{A_0} = (k_o - k_e)t \qquad (7)$$

As the oxidation proceeds, the product layer will become thicker. After some time interval, diffusion of oxygen through the product layer becomes the rate-controlling step. Suppose that the oxidation layer (with the thickness of x) can be divided into two layers. One layer (inside) contains B_2O_3 and ZCM with the thickness of x_1. The other (outside) containing only ZCM without B_2O_3 (evaporated) has the thickness of x_2, and $x= x_1 + x_2$. Due to the high porosity, resistance of diffusion through the outside layer is relatively very small. Then,

$$\frac{dw_o}{dt} = A_0 \Delta C \frac{D}{x_1} = A_0(\theta'\rho_{B_2O_3} - \theta\rho_{BN})\frac{dx}{dt} \qquad (8)$$

where: $\Delta C=C-C_i$, C_i is the content of oxygen at the interface. During the diffusion controlling step, C_i equals the equilibrium oxygen content; it is relatively very small, then $\Delta C=C$. D is the diffusion coefficient.

$$x_1 = x - x_2 = x - \frac{k_e t}{\theta'\rho_{B_2O_3}} \qquad (9)$$

$$\frac{dx_1}{dt} = \frac{dx}{dt} - \frac{k_e}{\theta'\rho_{B_2O_3}} \qquad (10)$$

Combination of equations (10) and (8) yields:

$$(\theta'\rho_{B_2O_3} - \theta\rho_{BN})\left(\frac{dx_1}{dt} + \frac{k_e}{\theta'\rho_{B_2O_3}}\right) = \frac{CD}{x_1} \qquad (11)$$

$$\frac{x_1 dx_1}{\dfrac{CD}{\theta'\rho_{B_2O_3} - \theta\rho_{BN}} - \dfrac{k_e}{\theta'\rho_{B_2O_3}} x_1} = dt \qquad (12)$$

$$\frac{\theta'\rho_{B_2O_3}}{k_e}\left(\frac{1}{1 - \dfrac{k_e(\theta'\rho_{B_2O_3} - \theta_{BN})}{CD\theta'\rho_{B_2O_3}} x_1} - 1\right) dx_1 = dt \qquad (13)$$

Integration of (13) yields:

$$-x_1 - \frac{cD\theta'\rho_{B_2O_3}}{k_e(\theta'\rho_{B_2O_3} - \theta\rho_{BN})} \ln\left(1 - \frac{k_e(\theta'\rho_{B_2O_3} - \theta\rho_{BN})}{CD\theta'\rho_{B_2O_3}} x_1\right)$$
$$= \frac{k_e}{\theta'\rho_{B_2O_3}} t \qquad (14)$$

As can be seen from equation (14), while time $t \to \infty$, then proximately

$$\frac{k_e(\theta'\rho_{B_2O_3} - \theta\rho_{BN})}{CD\theta'\rho_{B_2O_3}} x_1 = 1 \qquad (15)$$

As can be seen from (15), after some time interval, x_1 is constant, and

$$k_o = \frac{d(\Delta w_o/A_0)}{dt} = \frac{CD}{x_1} = \frac{(\theta'\rho_{B_2O_3} - \theta\rho_{BN})}{\theta'\rho_{B_2O_3}} k_e$$
$$= \text{Constant} \qquad (16)$$

$$\frac{d(\Delta w/A_0)}{dt} = k_o - k_e = \frac{-\theta\rho_{BN}}{\theta'\rho_{B_2O_3}} k_e \qquad (17)$$

Therefore, if the oxidation duration is long enough, the oxidation rate, as well as the evaporation rate, will be constant. From the slope of oxidation curves, k_e can be attained at different temperatures by equation (17). Thus the weight gain by oxidation (after correction by evaporation of B_2O_3) can be calculated at different temperatures. The results are shown in Fig.6.

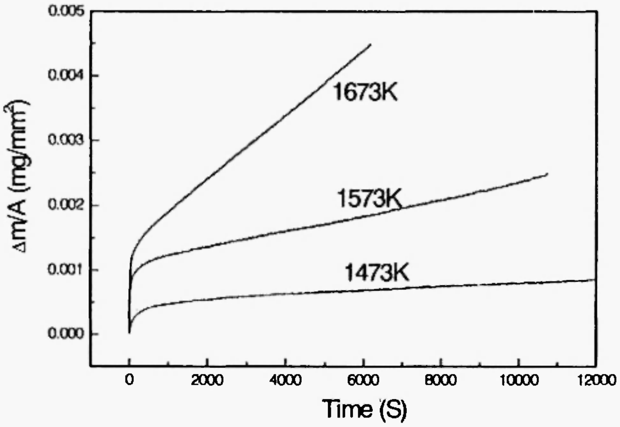


Fig. 6: Oxidation of BN-ZCM plate

From the initial period of Fig.6, k_c (k_o during the chemical reaction controlling step) can be obtained and the activation energy E_c can be calculated with an Arrhenius equation. As can be seen from Fig.7, E_c=254 kJ/mole. Assuming that the rate of B_2O_3 evaporation is relatively small at the beginning of oxidation, E_c can also be obtained from Fig.2 and it is 232 kJ/mole, slightly lower than the results from Fig.7. The effect of B_2O_3 evaporation may contribute to this difference.

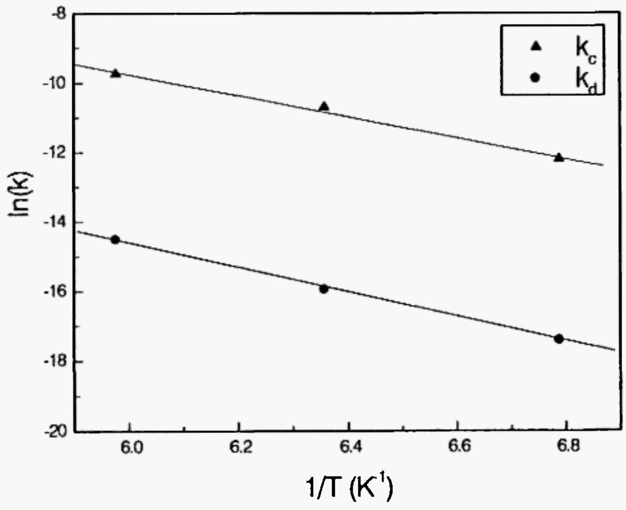


Fig. 7: The relations of ln(k) and 1/T of BN-ZCM

After some time interval, as the diffusion is the controlling step, x_l is constant and the oxidation degree is proportional to the time. Thus, the rate constant k_d (k_o during diffusion controlling step) can be attained at each temperature from Fig.6, and the overall activation energy $E_{d.}$ for oxygen diffusion can be calculated from Fig.7, E_d=289 kJ/mole. The high value of oxygen diffusion activation energy may be caused by the evaporation of B_2O_3.

4. CONCLUSION

The oxidation of BN-ZCM is a complicated process. At high temperatures, BN will be oxidized into B_2O_3. Simultaneously, B_2O_3 will evaporate into air because of its high equilibrium pressure. The large porosity of the evaporation layer allows further oxidation. This makes BN-ZCM a non-protective oxidation. Therefore, the atmosphere should be taken into account in application of BN-ZCM.

XRD analysis of oxidation layer shows that B_2O_3 is produced during the oxidation process. However, due to the evaporation of B_2O_2, the main crystal phases are Al_2O_3 and ZrO_2.

AFM (atomic force microscope) analysis shows that, as oxidation temperature increased from 1473 to 1673K, the roughness degree of the surface increases greatly from 63 to 406μm because of the evaporation of B_2O_3.

The overall activation energy of the chemical reaction is 254 kJ / mole and the overall activation energy of diffusion is 289 kJ / mole.

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