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Oxidation kinetics of hexagonal boron nitride powder

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The isothermal oxidation of hexagonal boron nitride powders was carried out at 900–1050 °C in dry oxygen and air. The oxidation kinetics were found to obey linear rate law and were described by the surface chemical reaction-controlled shrinking cylindrical model. The apparent activation energies were found to be 298 and 330 kJ mol^{-1} in dry oxygen and air, respectively. The oxygen partial pressure dependence of the oxidation rate constant at 1000 °C is well represented by a Langmuir-type equation. Microscopic examination of the oxidized sample after removal of the oxide scale with water suggested that the rate of attack by oxygen was determined by an anisotropy due to the crystallographic direction, similar to oxidation in graphite. The volatilization of B_2O_3 was observed only in dry oxygen and obeyed a linear rate law, and was found not to affect the oxidation reaction.

1. Introduction

Boron nitride (BN) is well known as one of the important engineering ceramics, with excellent chemical resistance and highly thermal stability. The structural forms and physical characteristics of BN are analogous to those of carbon in each modification. Recently, hexagonal boron nitride (h-BN) has been employed as a raw material of ceramic composites, where it has the function of improving the machinability and the thermal shock resistance. Therefore, it is important to investigate the oxidation behaviour of BN at high temperatures for determining its tolerable range for applications.

Many studies on the oxidation behaviour of BN at high temperatures have been conducted [1–5], but few studies on oxidation kinetics have been performed [3–5]. In general, oxidation behaviour essentially depends on chemical stability and the physical properties of the oxidation products. It is substantially recognized that B_2O_3 is characterized by fusibility, low viscosity and volatility. Therefore, it is necessary to evaluate, in terms of reacted fraction of BN, the oxidation kinetics, in addition to the weight change of sample, accompanying the volatilization of B_2O_3.

The purpose of this study was to investigate the oxidation kinetics of h-BN powder at various oxygen partial pressures and to discuss the oxidation mechanism in relation to the volatilization of oxidation products, B_2O_3.

2. Experimental procedure

The commercial grade h-BN powder was used as the sample in this study. The grains of BN were of a roundish platy shape as observed by scanning electron microscopy (SEM). The surface area of the BN sample was 2.2 m^2 g^{-1}, as measured by the BET method. The BN sample was above 98% in purity and had a mean diameter of 10.4 μm.

The isothermal oxidation of BN was carried out using a horizontal silica tube furnace equipped with SiC heating elements. It had been exposed to the oxidation atmospheres consisting of dry Ar–O_2 mixture gas and dry air. The oxygen partial pressures (P_{O_2}) of the Ar–O_2 mixture gas varied from 1 kPa to 0.1 MPa by adjusting the mixing volume of both a purified dry argon gas (99.99%) and a purified dry oxygen gas (99.99%). Air was dried by passing through concentrated sulphuric acid and calcium chloride. The total gas pressure of each oxidation atmosphere was 0.1 MPa. The total gas flow rate measured by gas flow meter was 100 cm^3 min^{-1}.

A 200 mg sample of BN was placed in a highly purified Al_2O_3 crucible (28 mm diameter and 13 mm height), and which was placed at the centre of the silica reaction tube. The thermocouple used for the controlling temperature was situated close to the crucible in the reaction tube. Prior to the isothermal oxidation, the reaction tube was evacuated. After maintaining at desired temperature and time, the crucible was removed from the reaction tube and quickly cooled. The weight change of the sample before and after oxidation was measured using an electrobalance. The crystalline phase of the oxidized sample was determined by X-ray diffraction (XRD) analysis using nickel-filtered CuK_α radiation. After that, each oxidized sample was etched with hot distilled water (50 °C) for removing soluble oxide scale such as B_2O_3, and then was filtrated, dried and weighed in order to determine the net weight of unreacted BN. It was confirmed by means of XRD analysis and infrared absorption analysis that the treated sample only consisted of h-BN. The microstructure of the treated samples was observed by SEM.

3. Results and discussion

Fig. 1 shows the time dependence of weight change for a 200 mg sample of BN powder in dry oxygen and air. No noticeable weight change by oxidation was observed at a temperature less than 900 °C. The weight change of the oxidized sample in dry oxygen exhibited a complex behaviour, that is, weight loss of the sample in the early stage of oxidation followed by weight gain (Fig. 1a). That in dry air represented a linear weight gain with oxidation time (Fig. 1b).

Formation of B_2O_3 resulting from the oxidation of BN was confirmed by means of XRD in all runs. The reaction of BN with oxygen forms B_2O_3 and N_2 or NO [1, 4]. This should lead to a weight gain of the sample after oxidation, if B_2O_3 is not volatilized. The volatilization of B_2O_3 was reported in a study on volatilization from glass melts containing B_2O_3 [6, 7] and oxidation of BN [4, 5, 8]. This contributes to the weight change of the sample as weight loss. Therefore, it was considered that estimation of oxidation kinetics is required, in terms of the reacted fraction measured by weight for unreacted BN.

The reacted fraction of BN was calculated by dividing the measured weight of oxidized sample after removal of the oxide scale with water, by that of the sample before oxidation. Fig. 2 shows the time dependence of the reacted fraction for BN oxidized in dry oxygen (P_{O_2} = 0.1 MPa) and air. The kinetics of BN powder were found to obey a linear rate law, in the case less than 0.6 reacted fraction in dry oxygen (P_{O_2} = 0.1 MPa) and air. The oxidation rate of BN in dry oxygen was about five times that in dry air.

As a result of comparing the kinetic data with various rate equations, it was found that oxidation is best described by the surface chemical reaction-controlled shrinking cylindrical model, as in the following equation

$$1 - (1 - \alpha)^{1/2} = kt \qquad (1)$$

where α is the reacted fraction, k the rate constant, and t the oxidation time. Fig. 3 shows the plots of the rate-controlling regime for the shrinking model fitted to the oxidation data. The fitness is very good for this model in the case of less than about 0.6 reacted fraction.

From the slopes of the straight part of these lines, the oxidation rate constants, k, were determined. The Arrhenius plots of the oxidation rate constant are shown in Fig. 4. The apparent activation energies were found to be 298 and 330 kJ mol^{-1} in dry oxygen (P_{O_2} = 0.1 MPa) and dry air, respectively. Podobeda *et al.* [3] measured the oxidation of turbostratic BN powder by a derivatographic method under non-isothermal conditions, and reported the activation energy value (about 305 kJ mol^{-1}) to be most similar to the present values.

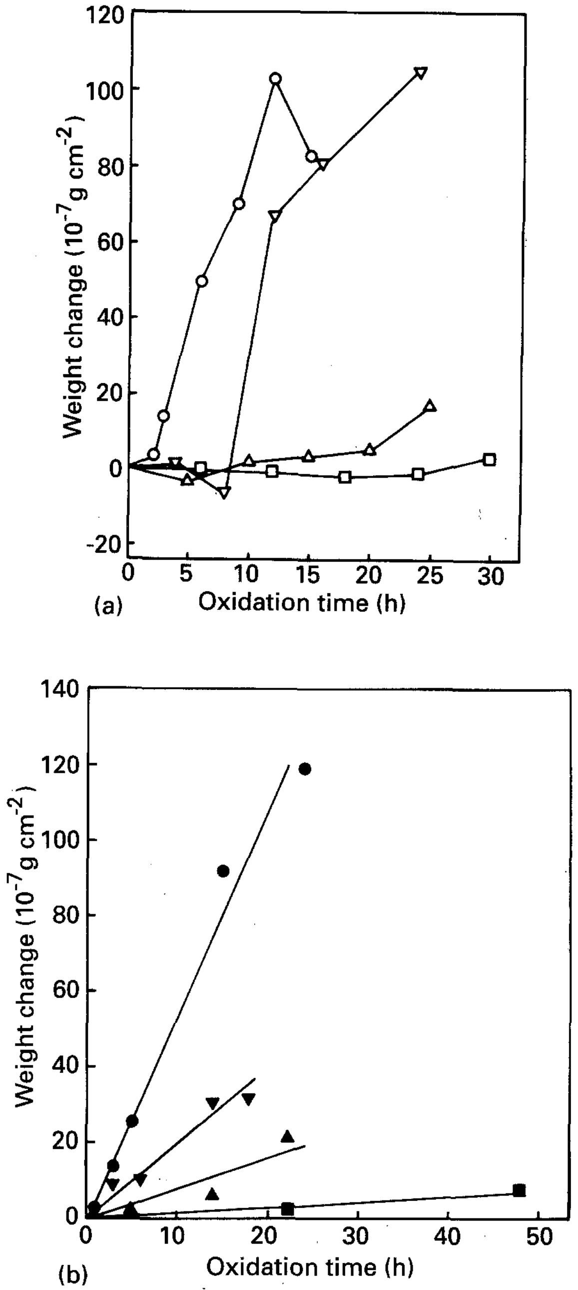

Figure 1 Time dependence of weight change for a 200 mg sample of BN powder oxidized (a) in dry oxygen and (b) in dry air. (○, ●) 1050 °C, (▽, ▼) 1000 °C, (△, ▲) 950 °C, (□, ■) 900 °C.

Fig. 5 shows the effect of P_{O_2} on the reacted fraction at 1000 °C as a function of oxidation time. The reacted fraction, at which is less than 0.6, increased linearly with oxidation time. From the slopes of the relation between $1 - (1 - \alpha)^{1/2}$ and oxidation time, the oxidation rate constants, k, at various P_{O_2} were determined. Fig. 6 shows the P_{O_2} dependence of the rate constant at 1000 °C. This plot is well represented by an expression of the Langmuir-type equation

$$k = aP_{O_2}/(1 + bP_{O_2}) \qquad (2)$$

where k is the oxidation rate constant, P_{O_2} oxygen partial pressure, and a, b are constants. Therefore, it was suspected that the oxidation of BN is dependent on the adsorbed fraction of oxygen molecules on the surface and is controlled by the surface reaction between oxygen and BN.

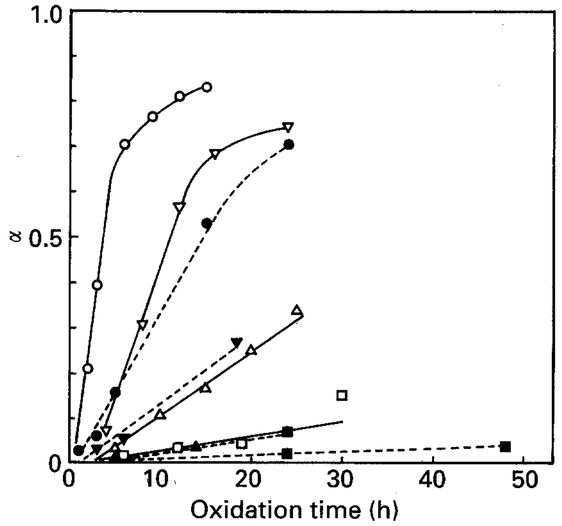

Figure 2 Time dependence of the reacted fraction for BN powder oxidized in (——) dry oxygen and (---) dry air. (●, ○) 1050 °C, (▽, ▼) 1000 °C, (△, ▲) 950 °C, (□, ■) 900 °C.

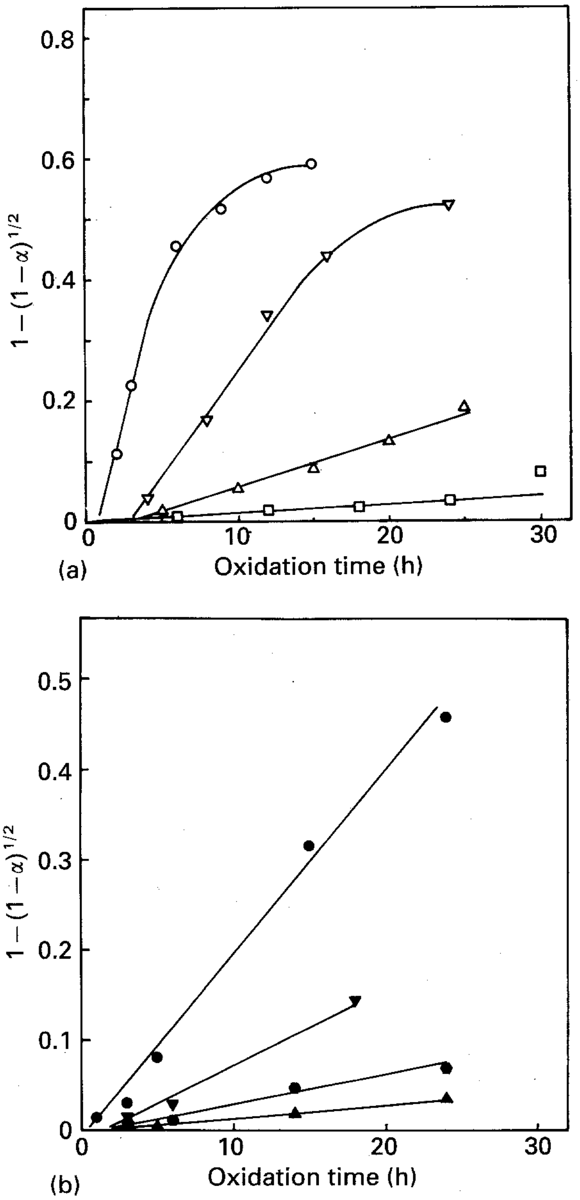

Figure 3 Plots of the rate-controlling regime for shrinking model applied to the oxidation data (a) in dry oxygen and (b) in dry air. (○, ●) 1050 °C, (▽, ▼) 1000 °C, (●) 975 °C, (△, ▲) 950 °C, (□) 900 °C.

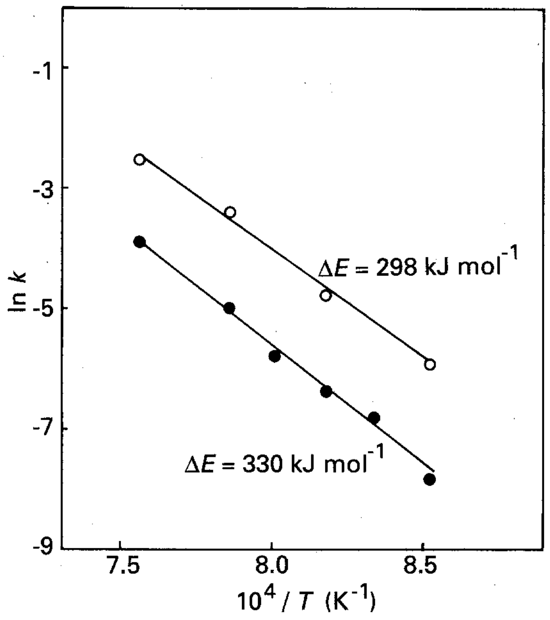

Figure 4 Arrhenius plots of the oxidation rate constants for BN powder in (○) dry oxygen and (●) dry air.

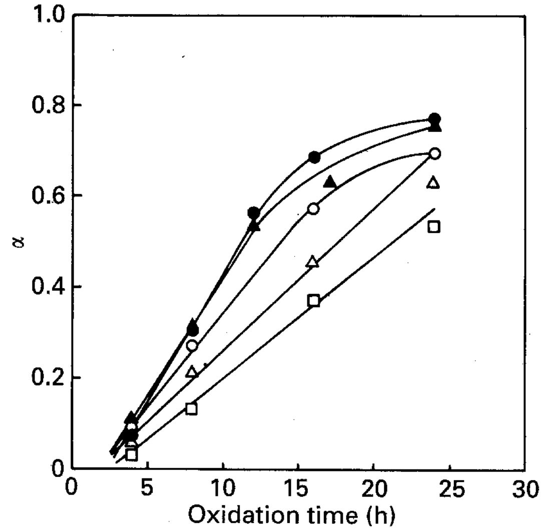

Figure 5 The effect of oxygen partial pressures (P_{O_2}) on the reacted fraction at 1000 °C as a function of time. (●) 1×10^{-1} MPa, (▲) 0.46×10^{-1} MPa, (○) 0.19×10^{-1} MPa, (△) 0.05×10^{-1} MPa, (□) 0.01×10^{-1} MPa.

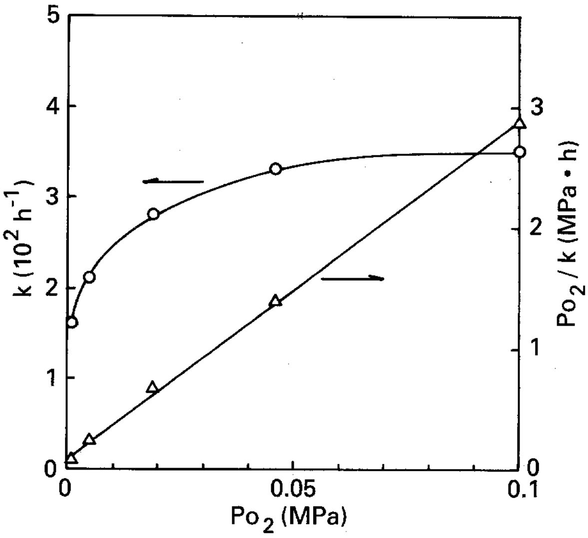

Figure 6 The P_{O_2} dependence of the oxidation rate constant at 1000 °C.

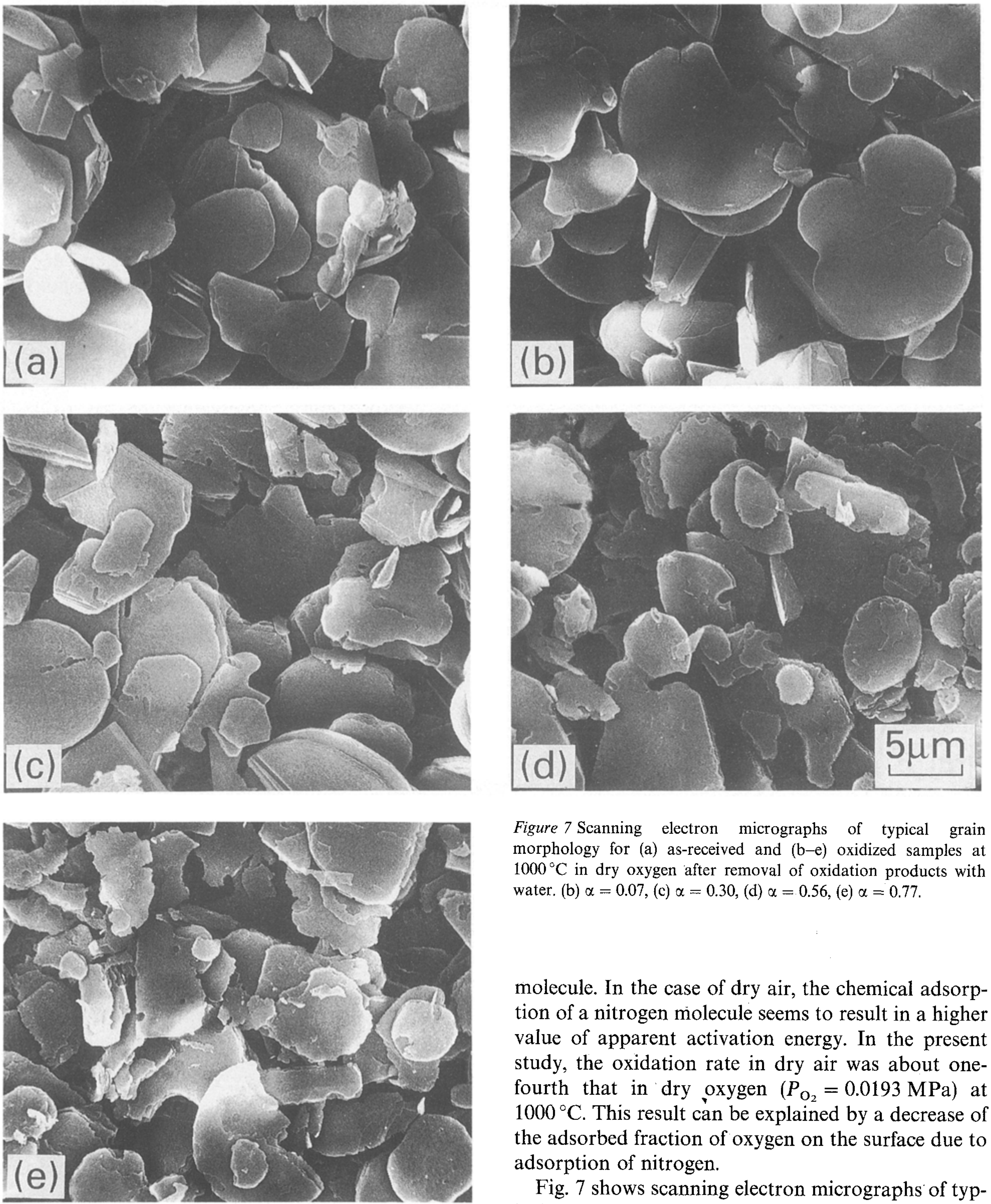

Figure 7 Scanning electron micrographs of typical grain morphology for (a) as-received and (b–e) oxidized samples at 1000 °C in dry oxygen after removal of oxidation products with water. (b) $\alpha = 0.07$, (c) $\alpha = 0.30$, (d) $\alpha = 0.56$, (e) $\alpha = 0.77$.

It seemed that those apparent activation energies obtained in the present study correspond to the B–N bond energy (433 kJ mol^{-1}), although a considerable difference between their values exists. If the rate-controlling step for the oxidation of BN was the diffusion of oxygen through B_2O_3 melts, then the apparent activation energy value would be around 137 kJ mol^{-1}, as reported by Tokuda *et al.* [9]. The difference between their values can be explained by the apparent activation energy, E_a, being obtained by the gap between the true activation energy, E_t, and the chemical adsorption enthalpy of the oxygen molecule. In the case of dry air, the chemical adsorption of a nitrogen molecule seems to result in a higher value of apparent activation energy. In the present study, the oxidation rate in dry air was about one-fourth that in dry oxygen ($P_{O_2} = 0.0193$ MPa) at 1000 °C. This result can be explained by a decrease of the adsorbed fraction of oxygen on the surface due to adsorption of nitrogen.

Fig. 7 shows scanning electron micrographs of typical grain morphology for (a) as-received and (b–e) oxidized samples in dry oxygen at 1000 °C for various oxidation times, after removal of the oxidation products with water.

A roundish platy shape was observed for as-received sample. The grain size has a mean diameter of 10.5 μm. As oxidation progresses, the grain sizes become smaller, mainly in the *a*-axis direction. The grain size of the sample oxidized for 24 h (Fig. 7e) has a mean diameter of about 5 μm with a reacted fraction of 0.77. In addition, the oxidized samples become angular or irregular in shape. These similar trends were observed in dry air. It is supposed that the oxidation of BN was exactly expressed by the oxidation rate Equation 1. These results suggest that the

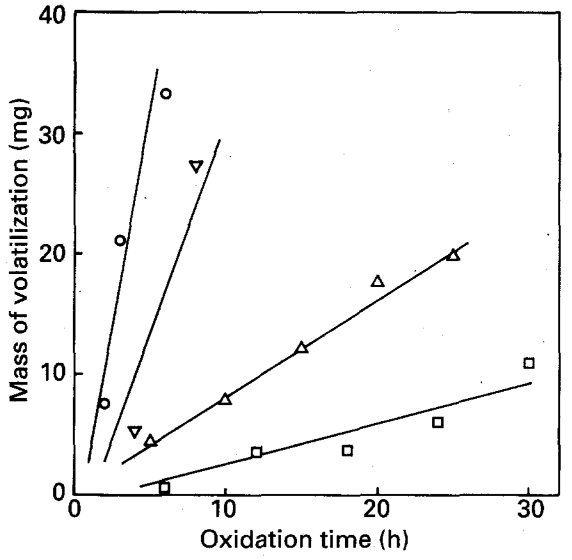

Figure 8 The mass of volatilized B_2O_3 on oxidation in dry oxygen as a function of time. (○) 1050 °C, (▽) 1000 °C, (△) 950 °C, (□) 900 °C.

rate of attack by oxygen is determined by an anisotropy due to the crystallographic direction.

The mass of B_2O_3 volatilized on oxidation was calculated from both the measured weight change and the theoretical amount of produced B_2O_3, calculated from the reacted fraction by assuming the conversion of BN to B_2O_3 according to the equation

$$2BN + 3/2O_2 = B_2O_3 + N_2 \qquad (3)$$

Fig. 8 shows the mass of B_2O_3 volatilized on oxidation in dry oxygen as a function of time. In the case of dry air, that was negligible within this temperature range. The mass of B_2O_3 still approximately increased linearly with oxidation time in each oxidation temperature. The mass of B_2O_3 volatilized was linear to the oxidation time in which the reacted fraction is relatively low. The observed volatilization rates were slightly higher than those of B_2O_3 melts [7].

The apparent activation energy for volatilization of B_2O_3 in dry oxygen ($P_{O_2} = 0.1$ MPa) was found to be 325 kJ mol^{-1}, similar to the heat of evaporation of B_2O_3 (326 kJ mol^{-1}) [10]. It was reported that the kinetics of evaporation of B_2O_3 melts obey a linear rate law and the reaction is zero-order reaction [7]. Therefore, it might be considered that the oxidation reaction of BN is not affected by the volatilization of B_2O_3.

4. Conclusions

1. The oxidation kinetics were found to obey a linear rate law and could be described by a surface chemical reaction-controlled shrinking cylindrical model.

2. The apparent activation energies were found to be 298 and 330 kJ mol^{-1} in dry oxygen and dry air, respectively, which were considered to correspond to the B–N bond energy.

3. The oxygen partial pressure dependence of the oxidation rate constant, was well represented by a Langmuir-type equation.

4. Microstructural observation of the oxidized sample revealed that the rate of attack by oxygen was determined by an anisotropy due to the crystallographic direction.

5. The volatilization of B_2O_3 was represented by a linear rate law in dry oxygen and was not observed in dry air, and did not affect the oxidation reaction under the experimental conditions studied.

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