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High-temperature oxidation of silicon nitride-based ceramics by water vapour

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Hot-pressed Si_3N_4, sintered Si_3N_4 and three kinds of sialon with different compositions were oxidized in dry air and wet nitrogen gas atmospheres at 1100 to 1350° C and 1.5 to 20 kPa water vapour pressure. All samples were oxidized by both dry air and water vapour at high temperature, and formed oxide films consisting of SiO_2, $Y_2Si_2O_7$ and $Y_4Al_2O_9$. The oxidation rate was in the order sialon > sintered Si_3N_4 > hot-pressed Si_3N_4. The oxidation rate of sialon increased with increasing Y_2O_3 content, and oxidation kinetics obeyed the usual parabolic law. The oxidation rates in dry air and wet nitrogen were almost the same: the rate in wet nitrogen was unaffected by water vapour pressure above 1.5 kPa. The activation energy was about 800 kJ mol^{-1}.

1. Introduction

Because of the superior physical and chemical properties such as high-temperature strength, resistance to thermal shock and resistance for corrosion, Si_3N_4-based ceramics have been leading candidates for high-temperature structural application. However, Si_3N_4-based ceramics are inherently unstable in oxidizing atmospheres. Many papers have been devoted to the kinetics of the oxidation of Si_3N_4-based ceramics in air at high temperatures [1–11]. The oxidation proceeds above 700 to 1000° C accompanied by the formation of oxide films consisting of SiO_2 and other oxides derived from the sintering additives, together with accidental impurities. Most of the previous workers reported that although the plots of weight gain against time approximate the usual parabolic behaviour, the oxidation rate was limited by the rate of outward diffusion of cations such as Mg^{2+} and Y^{3+} through an unoxidized substrate layer into the oxide film, but not by the rate of diffusion of the constituent element through the oxide film. The mechanism was supported by the experimental results that the oxidation rate is relatively unaffected by oxygen pressure [2, 5, 6] and by removal of the initial surface oxide scale [5, 6].

Several factors such as impurity content, porosity and humidity may affect the oxidation rate. Singhal [1] reported that the oxidation of hot-pressed Si_3N_4 was promoted by the presence of water vapour. However, the role of water vapour on the oxidation of Si_3N_4-based ceramics has not been clarified in detail. In the present study, a series of tests was carried out to evaluate the oxidation resistance of Si_3N_4-based ceramics in humid atmospheres using Si_3N_4 and sialon-doped with various amounts of Y_2O_3.

2. Experimental procedures

Hot-pressed Si_3N_4, sintered Si_3N_4 and three kind of sintered sialon, denoted as HP-Si_3N_4, S-Si_3N_4, SiAlON-1, SiAlON-2 and SiAlON-3, respectively, were used as oxidation samples. The characteristics of these ceramics are summarized in Table I. HP-Si_3N_4, S-Si_3N_4 and SiAlON-1 were β-Si_3N_4 structure. On the other hand, SiAlON-2 and SiAlON-3 were mixtures of α-Si_3N_4 and β-Si_3N_4 structures. The amounts of α-Si_3N_4 determined by Gazzara's method [12] were 30 and 60% respectively.

TABLE I Characteristics of the Si_3N_4-based ceramics used

Sample	Phase	Concentration (wt %)			Density (g cm^{-3})
		Si	Al	Y	
HP-Si_3N_4	β	56	1.0	3.7	3.20
S-Si_3N_4	β	53	3.6	3.5	3.21
SiAlON-1	β	59	0.4	0.9	3.19
SiAlON-2	$\alpha + \beta$	57	2.1	1.6	3.22
SiAlON-3	$\alpha + \beta$	54	4.2	3.1	3.22

α: α-Si_3N_4 type, β: β-Si_3N_4 type.

The diagram of the experimental apparatus used was shown in a previous paper [13]. All samples were cut into rectangular coupons, 2 mm × 10 mm × 10 mm and weighed. The specimens were placed in a horizontal tubular electric furnace regulated at the desired temperature. Controlled humid air or nitrogen gas was injected into the furnace at a rate of 20 ml min^{-1}. After maintaining the desired temperature and time, the specimen was withdrawn from the furnace and quickly cooled to room temperature, and then weighed. The crystalline phase and microstructures on the surface of the oxidized samples were examined by X-ray diffraction analysis and scanning electron microscopy. The partial water vapour pressure was adjusted to 1.5, 5, 10 and 20 kPa by bubbling air or nitrogen gas through the saturated aqueous solution of $Ca(NO_3)_2 4H_2O$ at 25° C and distilled water at 33, 46 and 60° C, respectively.

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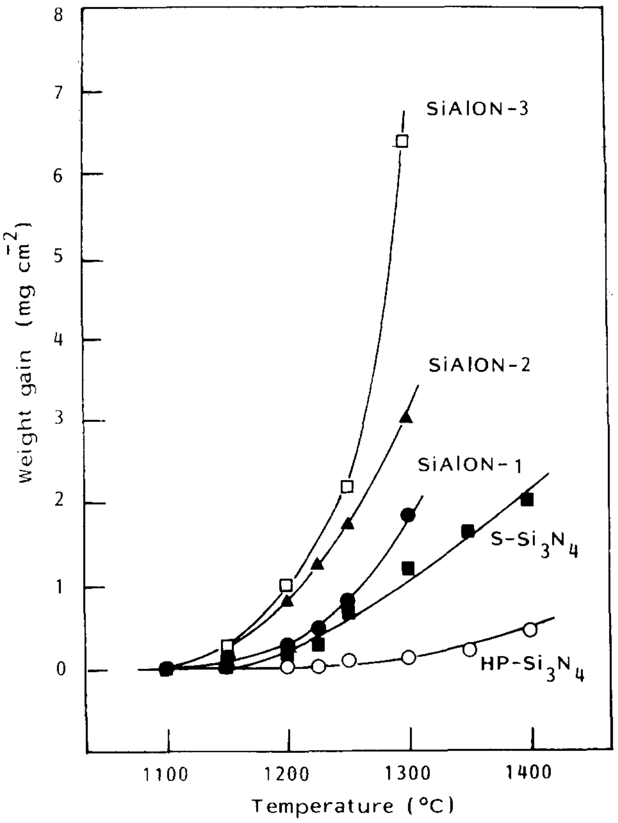

Figure 1 Temperature dependence of the weight gain of Si_3N_4-based ceramics in wet nitrogen gas atmosphere at 20 kPa water vapour pressure for 25 h.

3. Results and discussion

Although various reactions are thermodynamically possible to proceed in the Si_3N_4–H_2O system, the following reaction seemed to be the most probable:

$$Si_3N_4 + 6H_2O = 3SiO_2 + 2N_2 + 6H_2$$

The weight gain of each specimen after the oxidation in wet nitrogen at 20 kPa water vapour pressure and various temperatures for 25 h is shown in Fig. 1. Oxidation proceeded above 1150° C, and no noticeable weight change was observed at 1100° C for all specimens. The rate of oxidation was in the order SiAlON-3 > SiAlON-2 > SiAlON-1 > S-Si_3N_4 > HP-Si_3N_4. It has been reported that the oxidation resistance of Si_3N_4-based ceramics increased with increasing Al^{3+} content [4], but decreased with increasing Y^{3+} [7] and Mg^{2+} [9] contents. As seen in Table I and Fig. 1, the oxidation rate of SiAlONs increased with increasing Y^{3+} content. However, no relation was observed between the Y^{3+} content and the oxidation rate of HP-Si_3N_4, S-Si_3N_4 and SiAlON-1 with β-Si_3N_4 structure. These results indicated that not only the Y^{3+} content but also the composition of the glassy phase at the grain boundary might affect the oxidation rate, but details have not yet been clarified.

The scanning electron micrographs of the cross-sections of S-Si_3N_4, SiAlON-1 and SiAlON-3 oxidized in wet nitrogen at 1300° C and 10 kPa for 100 h are shown in Fig. 2. Oxide scales formed by the oxidation were observed on the surface. The scales on S-Si_3N_4 and SiAlON-1 have a glassy appearance with many pores, indicating that gas was trapped in the scale. On the other hand, the scale on SiAlON-3 was more granular.

The XRD profiles on the surfaces of the oxidized specimens in wet nitrogen gas atmospheres are shown in Figs 3 to 7. The XRD peaks corresponding to α-cristobalite, $Y_4Al_2O_9$ and $Y_2Si_2O_7$ were observed in oxidized HP-Si_3N_4, S-Si_3N_4 and SiAlON-1. Si_2ON_2 was also formed in the S-Si_3N_4 oxidized at 1200° C and 20 kPa for 10 h. The peak strength corresponding to $Y_4Al_2O_9$ and $Y_2Si_2O_7$ increased with increasing degree of oxidation. These resuls indicated that the cations added as sintering aids, such as Y^{3+} and Al^{3+}, were concentrated in the oxide scale. On the other hand, the main peaks in XRD for SiAlON-2 and SiAlON-3 corresponded to α-cristobalite, although unknown peaks were also detected for SiAlON-2 oxidized at 1200° C and 20 kPa for 100 h.

The time dependence of the weight gain for S-Si_3N_4, SiAlON-1 and SiAlON-2 oxidized in air and nitrogen gas atmosphere at 1300° C and 10 kPa water vapour pressure is shown in Fig. 8. It is seen that the oxidation behaviour may be expressed by the usual parabolic equation of the weight gain against time

$$W^2 = kt + C$$

where W is the sample weight gain per unit area, k is

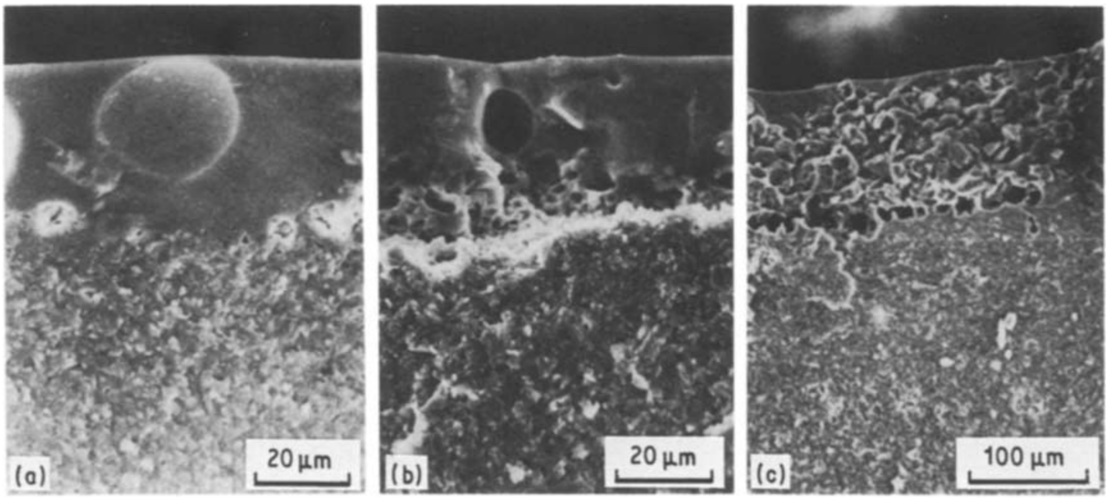

Figure 2 Scanning electron micrographs of the cross-sections of (a) S-Si_3N_4, (b) SiAlON-1 and (c) SiAlON-2 oxidized in wet nitrogen gas atmosphere at 1300° C and 20 kPa for 100 h.

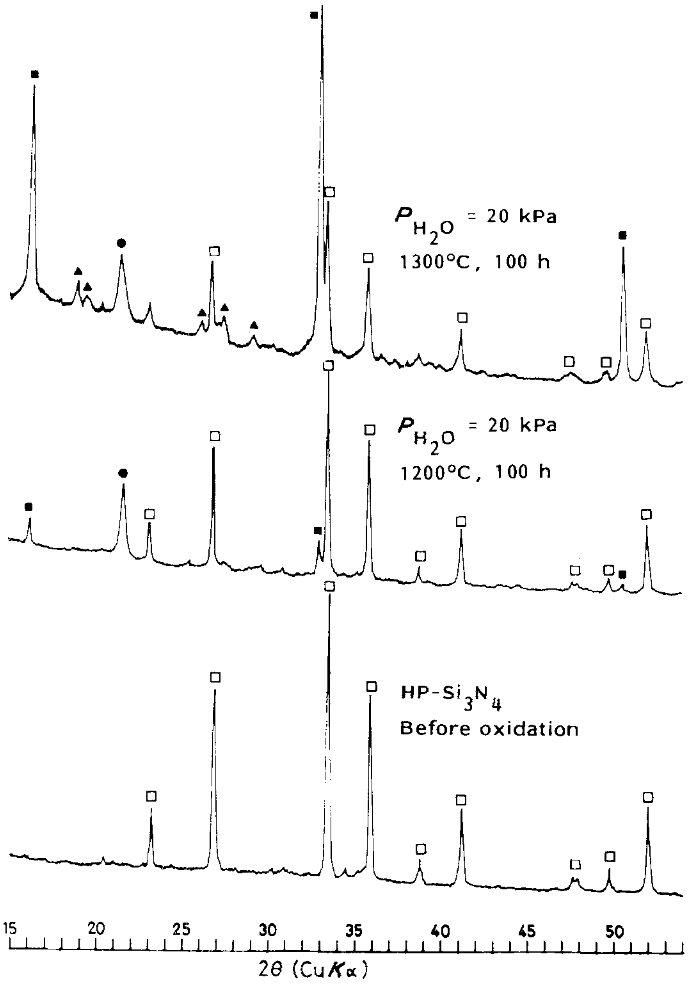

Figure 3 XRD profiles of oxidized HP-Si_3N_4. (●) α-cristobalite (SiO_2), (■) $Y_4Al_2O_9$, (▲) $Y_2Si_2O_7$, (□) β-Si_3N_4.

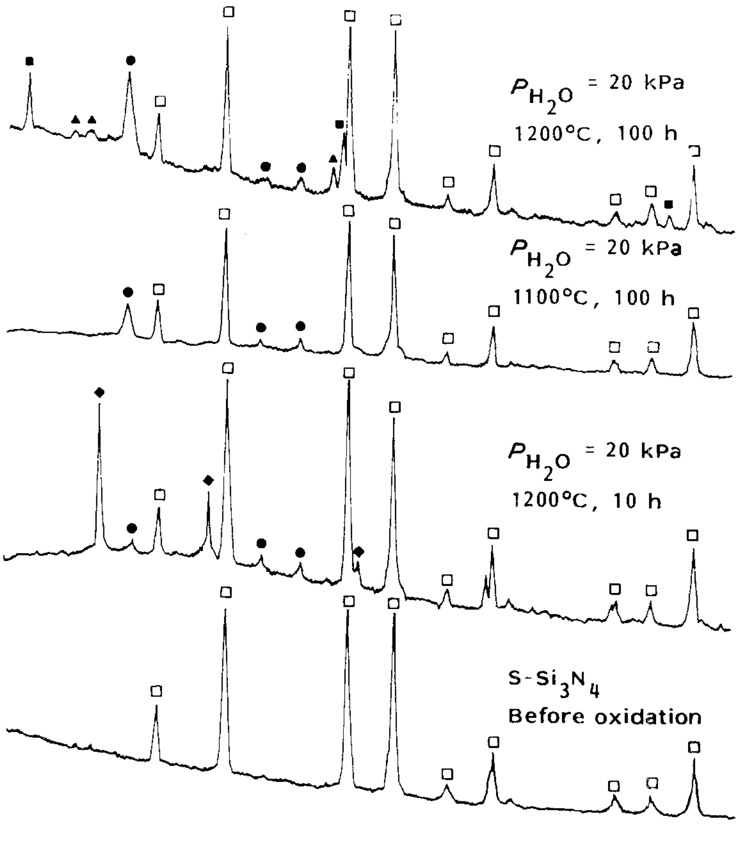

Figure 4 XRD profiles of oxidized S-Si_3N_4. (●) α-cristobalite (SiO_2), (■) $Y_4Al_2O_9$, (▲) $Y_2Si_2O_7$, (◆) Si_2ON_2, (□) β-Si_3N_4.

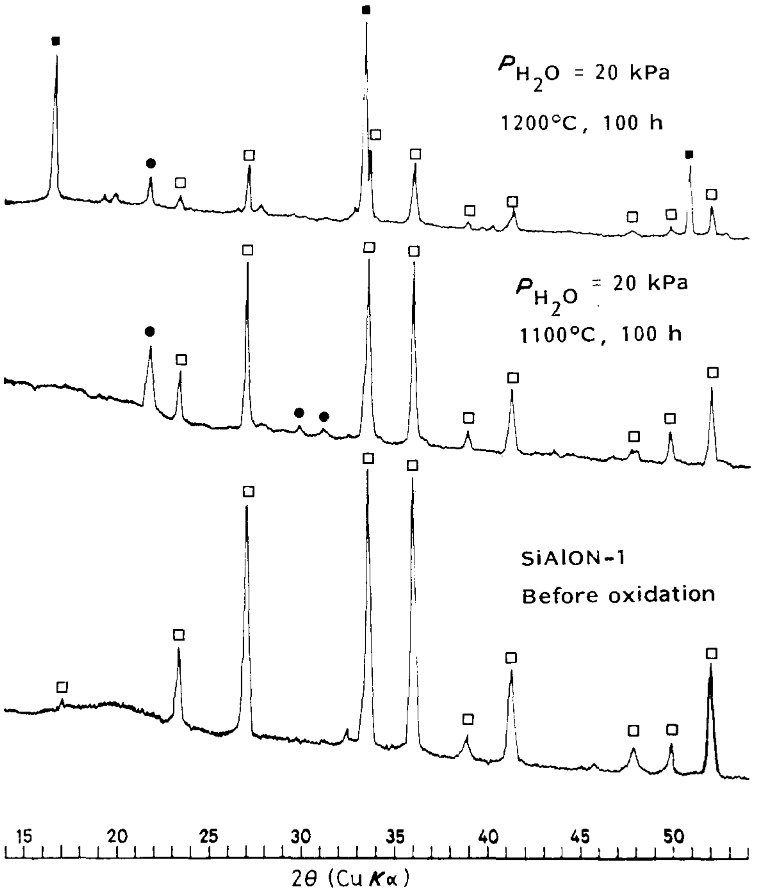

Figure 5 XRD profiles of oxidized SiAlON-1. (●) α-cristobalite (SiO_2), (■) $Y_4Al_2O_9$, (□) β-Si_3N_4 type.

the parabolic constant, t is the time and C is a constant to account for the initial nonparabolic reaction. It was notable that the rates of oxidation in dry air and wet nitrogen gas atmosphere were almost the same.

The humidity dependence of the parabolic rate constants for S-Si_3N_4, SiAlON-1, SiAlON-2 and SiAlON-3 oxidized at 1250° C is shown in Fig. 9. The oxidation rate was completely unaffected by the water vapour pressure above 1.5 kPa. These results indicated that the diffusion rate of water vapour, OH^- and O^{2-} through the oxide film does not control the oxidation rate.

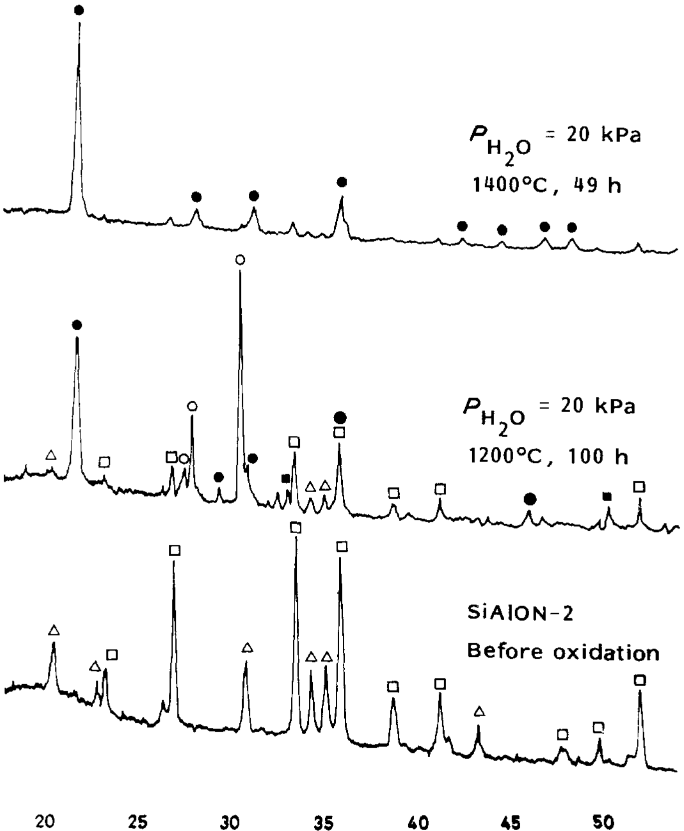

Figure 6 XRD profiles of oxidized SiAlON-2. (●) α-cristobalite (SiO_2), (■) $Y_4Al_2O_9$, (○) unknown, (△) α-Si_3N_4 type, (□) β-Si_3N_4 type.

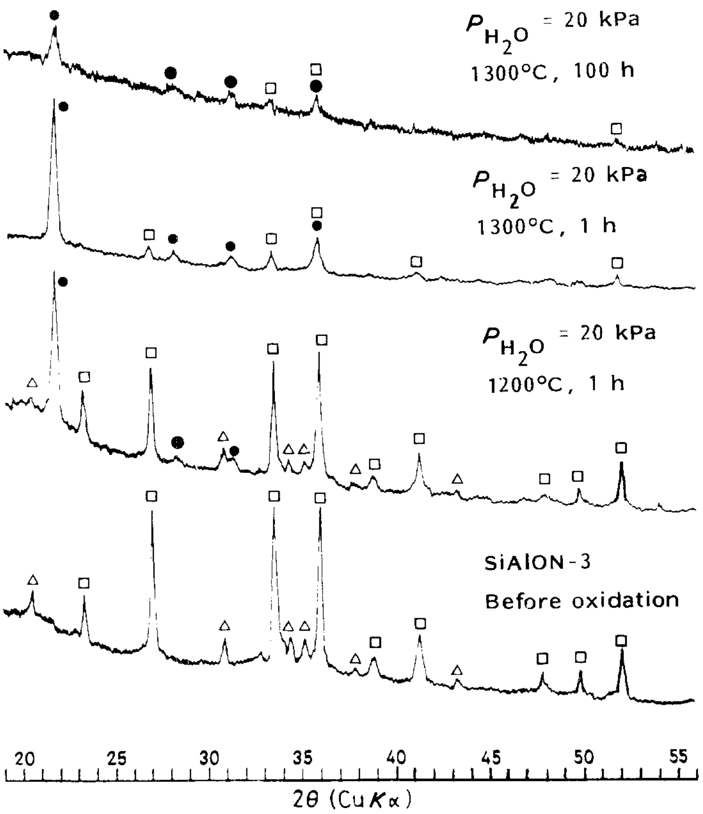

Figure 7 XRD profiles of oxidized SiAlON-3. (●) α-cristobalite (SiO_2), (△) α-Si_3N_4 type, (□) β-Si_3N_4 type.

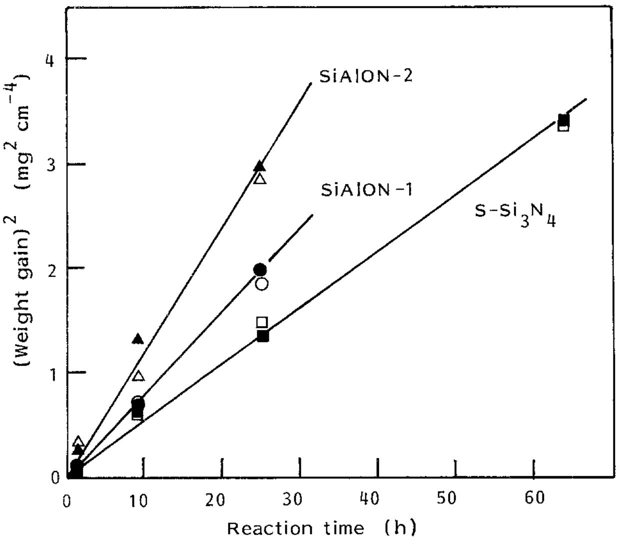

Figure 8 Time dependence of the weight gain of S-Si_3N_4, SiAlON-1 and SiAlON-2 oxidized in (□, ○, △) dry air and (■, ●, ▲) wet nitrogen with 20 kPa water vapour pressure at 1300° C.

Arrhenius plots of the parabolic rate constants for S-Si_3N_4, SiAlON-1, SiAlON-2 and SiAlON-3 oxidized in wet nitrogen gas atmosphere at 20 kPa are shown in Fig. 10. The apparent activation energies calculated were 724 to 809 kJ mol^{-1}, which were almost the same as that for the oxidation of Y_2O_3-doped Si_3N_4 ceramics in air [6, 11]. According to the present results, the mechanism of oxidation of Si_3N_4-based ceramics by water vapour seemed to be similar to that by air; namely, the oxidation rate was controlled by the diffusion rate of Y^{3+} through unoxidized substrate into the oxide film.

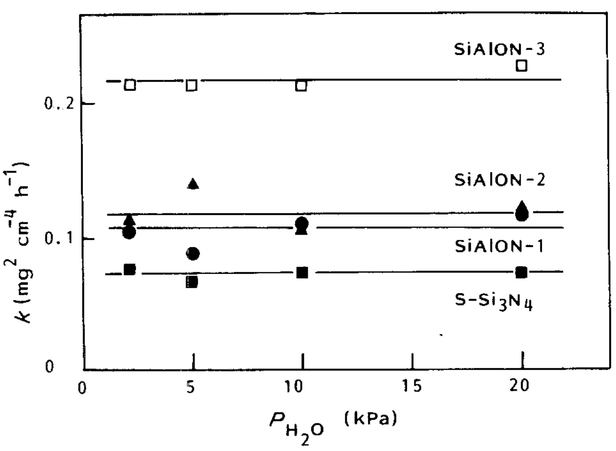

Figure 9 Humidity dependence of the parabolic rate constants of S-Si_3N_4, SiAlON-1, SiAlON-2 and SiAlON-3 in wet nitrogen at 1250° C.

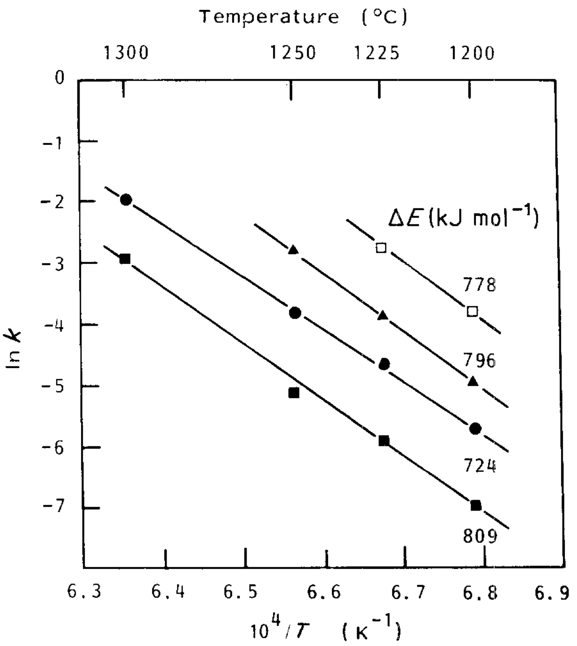

Figure 10 Arrhenius plots of the parabolic rate constants for (■) S-Si_3N_4, (●) SiAlON-1, (▲) SiAlON-2 and (□) SiAlON-3 in wet nitrogen atmosphere at 20 kPa.

4. Conclusions

1. The oxidation of Si_3N_4-based ceramics by water vapour proceeded above 1150° C.

2. The kinetics of the oxidation of Si_3N_4-based ceramics by water vapour was parabolic, and was unaffected by water vapour pressure above 1.5 kPa.

3. The outer diffusion of Y^{3+} through the unoxidized substrate into the oxide film seemed to control the rate of oxidation of Si_3N_4-based ceramics by water vapour.

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