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Effect of fluorine impurity on the oxidation of silicon oxynitride ceramics doped with gadolinium oxide

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Impurities in raw Si_3N_4 powders remain in intergranular glassy phases in Si_3N_4 and Si_2N_2O ceramics and degrade their high-temperature properties. Fluorine is one of the typical impurities in the raw powders. The oxidation rate of Si_2N_2O ceramics doped with Gd_2O_3 greatly varied with a difference in impurity contents (especially F) of the raw Si_3N_4 powders used. When a high concentration of impurity existed in the intergranular glassy phase, the rate of oxidation was controlled by O^{2-} diffusion through the glassy phase in the partly oxidized scale and unoxidized body; outward diffusion of Gd^{3+} occurred concurrently. On the other hand, when the impurity contents in the intergranular glassy phase was very low, the diffusion rate of ions (Gd^{3+}, O^{2-}, etc.) in the glassy phase became very low (substantially zero in the oxidation at 1300°C). Only cristobalite (SiO_2) was formed on the surface. The rate of oxidation was controlled by O_2 diffusion through the cristobalite layer, and was very low.

1. Introduction

Silicon oxynitride (Si_2N_2O) has been of interest as a promising engineering ceramic material for high-temperature applications because of its very low specific gravity (2.81 g/cm^3; the theoretical density of Si_2N_2O [1]), excellent oxidation resistance [2–6] and high strength at high temperatures [5, 6].

Si_2N_2O ceramics are produced by sintering an equimolar Si_3N_4 and SiO_2 powder mixture with additives. A liquid forms as a result of a reaction between all the constituents above a eutectic temperature. The liquid promotes densification and formation of Si_2N_2O. Although the liquid decreases in volume fraction as the formation of Si_2N_2O and crystallization in intergranular phases proceeds, some liquid remains as an intergranular glassy phase [7]. The intergranular glassy phase limits the potential properties (mechanical properties, oxidation behavior, etc.) of Si_2N_2O ceramics [5, 6, 8].

Pure Si_2N_2O is resistant to oxidation due to the formation of a SiO_2 layer on its surface, however, when Si_2N_2O ceramics with the residual intergranular glassy phase are oxidized, the oxidation is accelerated by the outward diffusion of cations originating from both additives and impurities through the glassy phase [5, 6]. Therefore, it is important for the oxidation of Si_2N_2O ceramics to control the chemical composition of the intergranular glassy phase.

A large amount of fluorine (F) is sometimes contained in raw Si_3N_4 powders as an impurity element. It remains and concentrates in the intergranular glassy phase even after sintering and affects the mechanical properties of Si_3N_4 sintered bodies at high temperatures [9]. F impurity also strongly influences the mechanical properties of Si_2N_2O ceramics [8]. In this study, two kinds of raw Si_3N_4 powders with different impurity contents, especially the F content, were used for investigation into the effect of impurities on the oxidation behavior of Si_2N_2O ceramics doped with Gd_2O_3.

2. Experimental procedure

The impurity contents in two kinds of starting Si_3N_4 powders (A and B) are summarized in Table I. Powder (A) contained larger amounts of impurities than powder (B). The F, Al and Ca contents in powder (A) were approximately 11 times, 7 times and three times as much as those in the powder (B), respectively. There were no appreciable differences in Fe, Mg, O, C and Cl contents between these powders. Starting oxide powders (SiO_2, Gd_2O_3,; Hokko Chemical Industry Co., Ltd. Tokyo, Japan) were derived from alkoxides and had a purity of more than 99.9%. The equimolar Si_3N_4/SiO_2 powder was mixed with Gd_2O_3 powder by a vibrational mill for 6 h in methanol using a silicon nitride container and balls. The starting compositions are given in Table II. DG15 was prepared from the relatively impure Si_3N_4 powder (A), and UG15 from the relatively pure Si_3N_4 powder (B). The amount of oxygen in the Si_3N_4 powders was counted as another SiO_2 source. In this study, the oxygen content of the Si_3N_4 powders was determined to be approximately 1.2 wt%, but they were

TABLE I Impurity contents in two kinds of raw Si_3N_4 powders (A and B)

	Fe	Al	Ca	Mg	Cl	F	O(%)	C(%)
A	55	75	20	3	36	1480	1.21	0.16
B	47	11	7	2	25	130	1.24	0.16

(in ppm)

TABLE II Starting compositions of Si_2N_2O ceramics in mass%

	Si_3N_4	SiO_2	Gd_2O_3
DG15, UG15	71.73	23.02	5.25

estimated to be more (4 wt%) by considering the effect of oxidation through processings when the starting compositions were calculated. After drying, the mixed powder was passed through a 60 mesh sieve and then hot-pressed under 29 MPa at 1750°C for 2 h in 0.1 MPa nitrogen atmosphere. The heating rate was 10°C/min.

Oxidation experiments were performed in a horizontal alumina tube furnace (1.96 l) equipped with SiC heating elements at 1300 and 1400°C in flowing dry air (0.65 l/min). The specimens dimensions were 3 × 3 × 26 mm bars. The specimens were weighed before and after the test at each temperature and time, using a balance with the accuracy of 0.01 mg.

Crystalline phases present were identified by an X-ray diffractometer (XRD) (Cu K_α, 40 kV, 100 mA). Backscattered electron images and x-ray images (Gd, O) of cross sections of the specimens after exposure in air at high temperature were observed using an electron probe microanalyzer (EPMA).

3. Results and discussion

DG15(2) and UG15(2) hot-pressed at 1750°C for 2 h consisted of Si_2N_2O, a small amount of β -Si_3N_4, and $Gd_5(SiO_4)_3N$, which were confirmed by XRD as the crystalline phases present. $Gd_5(SiO_4)_3N$ crystallized in the triple grain junctions at grain boundaries during cooling. However, the crystallization was not complete and a small amount of an intergranular glassy phase remained at the grain boundaries.

Figs 1 and 2 show the oxidation behavior of UG15(2) and DG15(2) exposed to dry air at 1300 and 1400°C. They almost exhibited parabolic rate kinetics, except for the initial incubation period. Therefore, the rate-determining step for oxidation is probably a diffusion process. Parabolic rate constants (K_p) for DG15(2) and UG15(2) were compared with those reported previously for hotpressed Si_3N_4 (HP-SN(MgO)) [10], CVD-Si_3N_4 (CVD-cSN, CVD-amSN) [11], pressureless-sintered SiC (S-SiC(B + C)) [12], pure Si_3N_4 powders (P- α SN, P- β SN) [13], and CeO_2-doped Si_2N_2O (SC30(1), SC30(2)) [5] as shown in Fig. 3. The oxidation rate of UG15(2) prepared from the relatively pure powder (B) was lower than B + C-doped SiC known as one of the non-oxide ceramics most resistant to oxidation. Fig. 4 shows the backscattered electron images and elemental distribution of gadolinium and oxygen

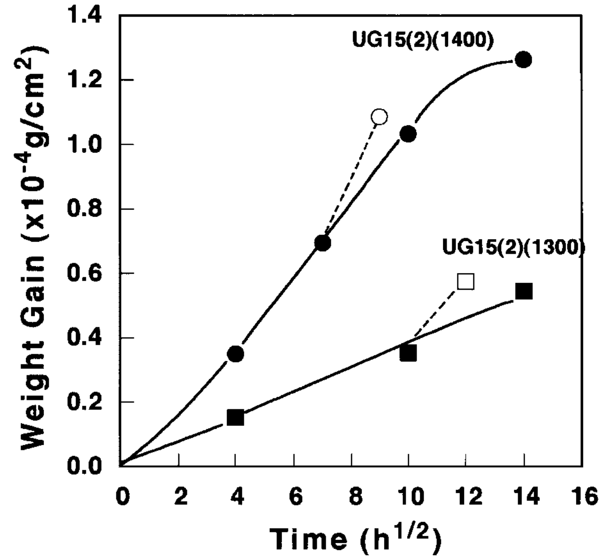

Figure 1 Weight gain of UG15(2) oxidized in dry air at 1300 and 1400°C (solid symbols). Open symbols are the points obtained by re-oxidation.

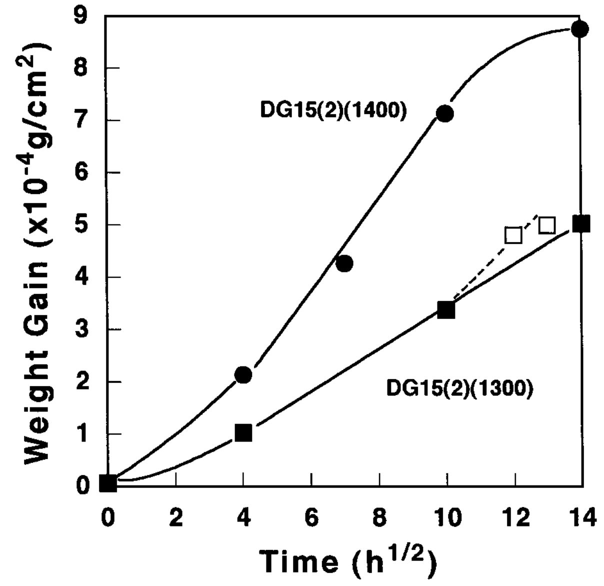

Figure 2 Weight gain of DG15(2) oxidized in dry air at 1300 and 1400°C (solid symbols). Open symbols are the points obtained by re-oxidation.

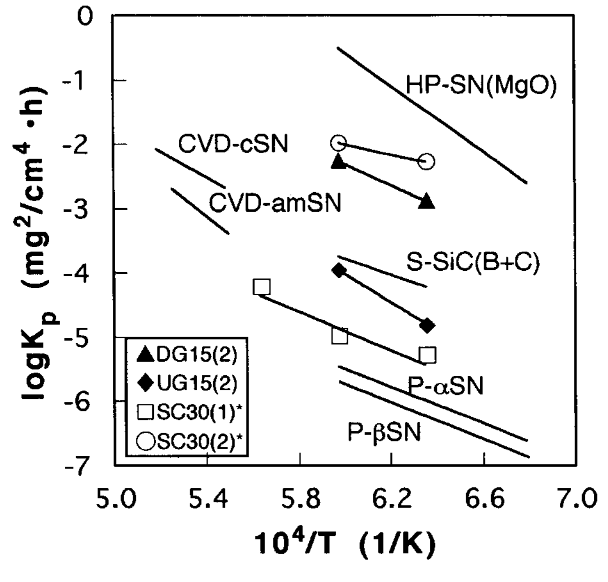

Figure 3 Parabolic rate constants for oxidation of various non-oxide ceramics: HP-SN(MgO) (ref. [10]), CVD-cSN, CVD-amSN (ref. [11]), S-SiC(B + C) (ref. [12]), P- α SN, P- β SN (ref. [13]).

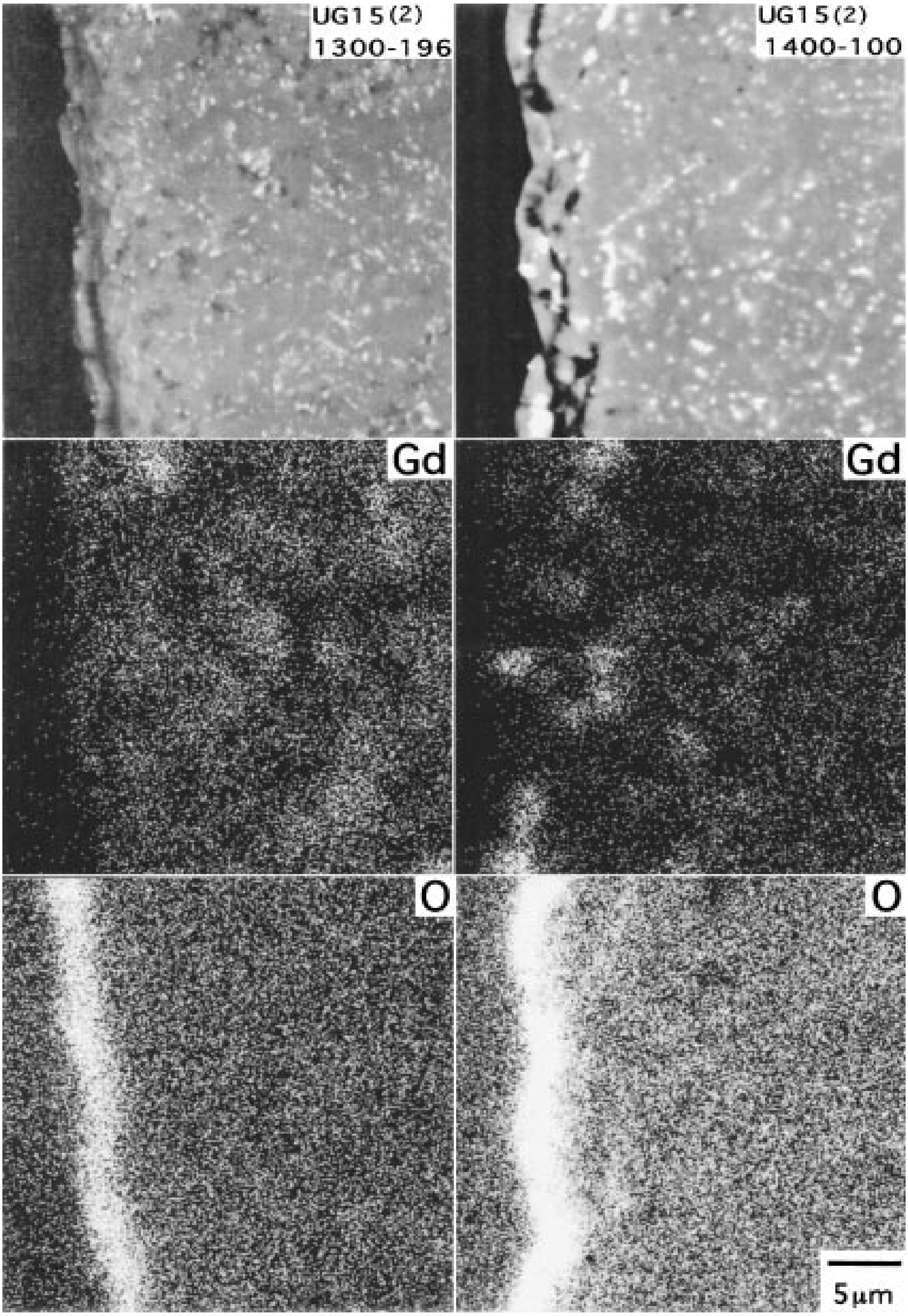

Figure 4 Backscattered electron images and elemental distribution of gadolinium and oxygen for cross sections of UG15(2) oxidized at 1300°C for 196 h and UG15(2) oxidized at 1400°C for 100 h.

for cross sections of UG15(2) oxidized at 1300°C for 196 h and UG15(2) oxidized at 1400°C for 100 h. The surface scale formed at 1300°C was composed of uniform and dense α -cristobalite. Gadolinium ions (Gd^{3+}) had hardly diffused through the residual intergranular glassy phase to the surface. This reveals that the diffusion rate of Gd^{3+} is very low in the intergranular glassy phase. However, Gd^{3+} diffused to the surface and precipitated as $Gd_2Si_2O_7$ at 1400°C, in addition to cristobalite.

A sample, oxidized at 1300°C at 100 h, was cooled to room temperature, a portion of the surface scale was

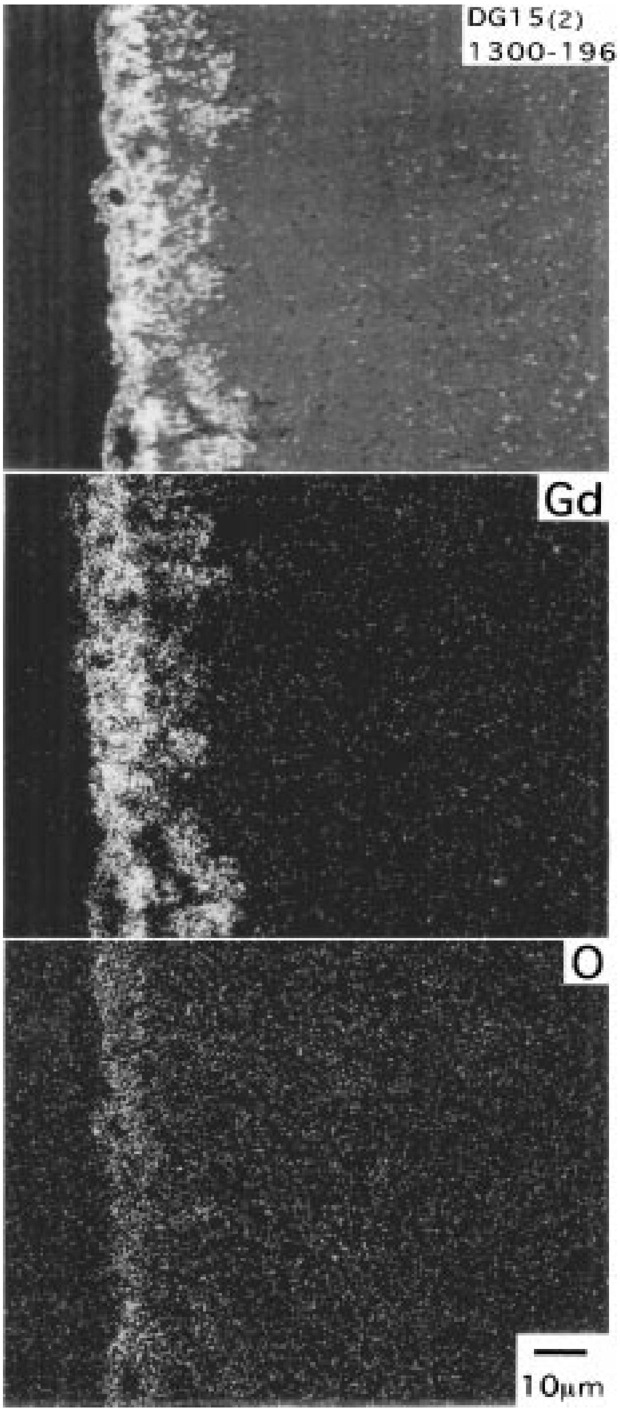

Figure 5 Backscattered electron image and elemental distribution of gadolinium and oxygen for cross section of DG15(2) oxidized at 1300°C for 196 h.

removed by surface grinding, and the sample was re-oxidized at 1300°C. This experiment was carried out for analysis of the oxidation mechanism of Si_3N_4 ceramics previously by Cubicciotti and Lau [14]. The same re-oxidation experiment was also performed for a sample oxidized at 1400°C for 64 h. The open circles in Fig. 1 are the points obtained by the re-oxidation. This result shows the scales to be protective against oxidation. The process controlling the oxidation rate could have been inward-diffusion of oxygen through the scales. In the case of the oxidation at 1300 to 1500°C for CeO_2-doped Si_2N_2O ceramics hot-pressed at 1750°C for 1 h, the oxidation scales were composed of only α -cristobalite [5] as observed for the oxidation of UG15(2) at 1300°C. An activation energy for the oxidation of the CeO_2-doped Si_2N_2O ceramics (which are shown in Fig. 3 as SC30(1)) was comparable to that for diffusion of oxygen molecules in fused silica. It is suggested that the diffusion of molecular oxygen in the cristobalite layer was the rate-determining step [5]. Therefore, the oxidation of UG15(2) at 1300°C were also presumed to be governed by the diffusion of molecular oxygen in cristobalite.

The oxidation rate of DG15(2) prepared from the relatively impure powder (A) containing a large amount of F was much higher than UG15(2) made from the pure powder (B) as shown in Fig. 3. Fig. 5 shows the backscattered electron image and elemental distribution of gadolinium and oxygen for the cross section of DG15(2) oxidized at 1300°C for 196 h. A large amount of $Gd_2Si_2O_7$ formed in the surface scale, in addition to cristobalite. It appears to result from a high outward-diffusion rate of Gd^{3+} through the residual intergranular glassy phase with high impurity content. Mass transport in DG15(2) during oxidation predominantly occurred via the intergranular glassy phase which had a high impurity concentration and high ion conductivities for Gd^{3+}, O^{2-}, etc.. No impurity ion, including F, was detected in the scale by EPMA.

The re-oxidation experiment was also performed for a sample oxidized at 1300°C for 100 h. The open circles in Fig. 2 were the points obtained by the re-oxidation. This result shows the scale to be also protective against oxidation. The process controlling the oxidation rate could have been inward-diffusion of O^{2-} through the residual intergranular glassy phase in the partly oxidized scales and unoxidized bodies.

Weight gains of UG15(2) and DG15(2) after oxidation at 1400°C for 196 h fell below the line which would be expected if the oxidation obeyed the parabolic law with the same rate constants as shown in Figs 1 and 2. Outward diffusion of Gd^{3+} occurred in both samples at 1400°C. Because large amounts of Gd^{3+} had already migrated to the scales after the prolonged oxidation at 1400°C and Gd contents in the center of the bodies probably decreased from their initial values, the oxidation rate constants decreased with time over 100 h.

4. Conclusions

The oxidation of Gd_2O_3-doped Si_2N_2O ceramics obeyed the parabolic rate law. The re-oxidation experiments showed that the oxidation scales were protective. Therefore, oxygen diffusion through the scales could have been the rate-determining step. However, the oxidation rate varied with a difference in impurity contents (especially F) of the raw Si_3N_4 powders used.

Fig. 6 shows schematic representations of the processes occurring in the oxidation mechanism. When high concentration of impurity existed in the intergranular glassy phase, the rate of oxidation was controlled by O^{2-} diffusion through the glassy phase in the partly oxidized scale and unoxidized body, and outward diffusion of Gd^{3+} occurred concurrently. On the other hand, when the impurity content in the intergranular glassy phase was very low, the diffusion rate of ions

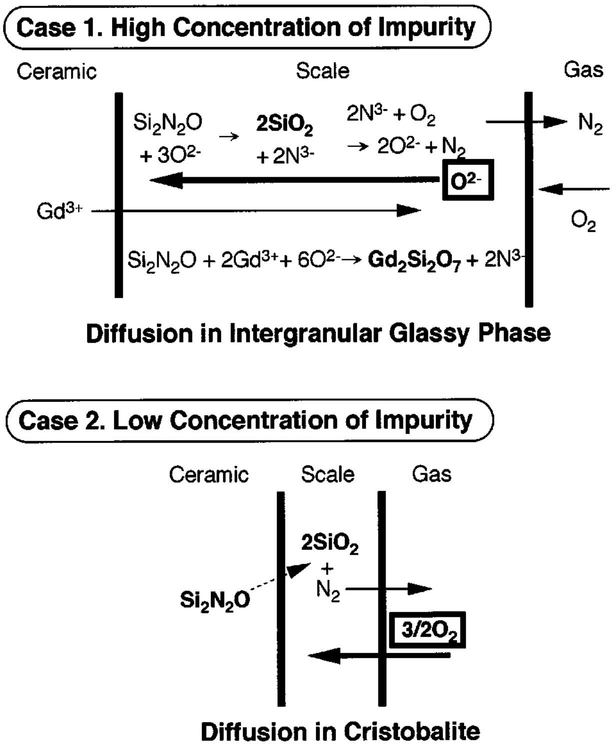

Figure 6 Schematics of reactions involved in oxidation mechanisms.

(Gd^{3+}, O^{2-}, etc.) in the glassy phase became very low (substantially zero in the oxidation at 1300°C). Si_2N_2O was directly oxidized and cristobalite (SiO_2) formed on the surface. Si_2N_2O was successively oxidized at the Si_2N_2O/SiO_2 interface. The rate of oxidation was controlled by O_2 diffusion through the cristobalite layer, and was very low.

The oxidation resistance and behavior of the Si_2N_2O ceramics doped with lanthanide oxide is sensitively influenced by impurity contents, especially F, in the raw Si_3N_4 powder.

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