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Oxidation of silicon nitride in a wet atmosphere

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The effect of water vapour on oxidation was studied with hot-pressed silicon nitride containing both yttria and alumina as sintering aids in wet air flow with 10, 20, 30, and 40 vol% H_2O at 1300° C for 100 h. The oxidation kinetics were determined in a wet air flow with 20 vol% H_2O and in a dry air flow at 1300° C for oxidation times up to 360 h. The water vapour in the atmosphere slightly influenced the oxidation and accelerated the reaction, and the weight gained on oxidation in a wet atmosphere had an increasing tendency with increasing water vapour content. The oxidation proceeded in a diffusion-controlled manner in both wet and dry atmospheres. The values of weight gained in wet oxidation varied to a greater degree than in dry oxidation. Water vapour had a strong effect on the devitrification of the amorphous oxide. This process was presumed to promote the rate of oxidation more than in dry atmosphere. The water vapour also had a strong roughening effect on the surface oxide layer grown during oxidation. The flexural strength at room temperature was degraded by oxidation in a wet atmosphere and it is presumed to be degraded by wet oxidation slightly and consecutively with time.

1. Introduction

Silicon nitride is a promising candidate for high-temperature engineering materials, because of its excellent thermomechanical properties and oxidation resistance. In particular, silicon nitride has a high strength and an excellent thermal-stock resistance at high temperatures.

On oxidation of silicon nitride in a dry atmosphere, a considerable number of studies [1-19] have been performed, but there have been few studies concerning the effect of water vapour on the oxidation of silicon nitride. Before silicon nitride is put to practical use, however, it is indispensable to investigate the effect of water vapour on the oxidation of silicon nitride, because it is usually applied in the atmospheric environment or in an atmosphere containing more or less water vapour.

Horton [20] reported that the observed oxidation rate in humid air was approximately twice that in dry air. Singhal [21] found that water vapour accelerated the oxidation of Si_3N_4 and SiC. However, he commented that in the oxidation of hot-pressed Si_3N_4 and SiC, various impurities, e.g. calcium, magnesium, sodium, potassium, etc., also caused devitrification of the surface glass; it is, thus, difficult to differentiate the effect of impurities and water vapour on devitrification.

Mayer and Riley [22] mentioned that the oxidation rates in dry air at each temperature were the same within experimental error as those in wet air, the small quantity of water vapour in normal atmospheric air did not appear to have a significant effect on the reaction rates, and the slight irregular differences observed could be attributed to experimental error.

These works on the oxidation behaviour of silicon nitride in a wet atmosphere have been concerned only with an atmosphere containing a small amount of water vapour and for a short time, and no comprehensive investigation of the oxidation behaviour has previously been carried out.

The present study was undertaken to characterize the oxidation behaviour of Y_2O_3 and Al_2O_3-containing hot-pressed silicon nitride under a higher humidity environment than atmospheric conditions and to elucidate the effect of water vapour on oxidation.

2. Experimental procedure

Oxidation kinetics were determined in wet and dry atmospheres at 1300° C of hot-pressed silicon nitride containing alumina and yttria as densifying aids.

2.1. Materials

Specimens were rectangular bars with dimensions 3 mm × 4 mm × 40 mm. The specimen surfaces were ground in the longitudinal direction with a 400-grit diamond wheel and the edges were bevelled at 45° by 0.2 mm in accordance with Japan Industrial Standard, JIS R1601 (Testing Method for Flexural Strength of High Performance Ceramics). The samples were cleaned ultrasonically in acetone and alcohol.

The bulk density was measured by the displacement method and ranged from 3.17 to 3.24 g cm^{-3}. The amounts of major components in the Si_3N_4 specimen other than silicon, as determined by chemical analysis, are shown in Table I.

2.2. Oxidation

The oxidation in a wet atmosphere was performed

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TABLE I Chemical analysis

	Al	Y	Mg
content (wt %)	0.82	2.69	0.006

using an electric tube furnace with a water vapour producer and hygrometer, and a schematic diagram of the apparatus is given elsewhere [23].

The humidity of air, bubbled into the water in the evaporator with the condenser by the air pump, was controlled by the electric power supply to the evaporator heater, and by adjusting the circulating water temperature of the water bath for the condenser.

The dew point of the wet air was measured using a hygrometer at a position just in front of the air inlet to the oxidation test furnace, and was monitored by a recorder. The water vapour contents in the air tested in this study were 10, 20, 30 and 40 vol %, and the air flow rate was 800 ml min^{-1}. The oxidation temperature was 1300° C and the time was 100 h for all experiments, except for the kinetic measurements. The kinetic measurements were carried out in two atmospheres; one was dry and the other was wet with 20 vol % water vapour. The oxidation time was up to 360 h (15 days) and the air flow rate was 800 ml min^{-1}. In the dry test, oxidation was done in flowing air after passing it through silica gel and dispersed phosphorous pentoxide drying towers. The specimens were placed on a pressureless-sintered silicon carbide setter and loaded in the centre of the furnace.

2.3. Sample characterization

The specimens were characterized by measuring the weight change before and after oxidation with a semimicro balance weighing to 0.01 mg, and by optical microscopy, scanning electron microscopy (SEM), electron probe microscope analysis (EPMA), and X-ray diffractometry (XRD).

The surface roughness of specimens before and after oxidation were measured by the contact profile method.

The strength distributions were determined on a four-point loading fixture with an outer span of 3.00 cm, and an inner span of 1.00 cm (one-third-point loading). All flexural strength testings were carried out at a cross-head speed of 0.5 mm min^{-1} at room temperature and the specimens were tested without any retouching of the surface after oxidation.

3. Results and discussion

3.1. Oxidation in a wet atmosphere

The weight gained on oxidation of silicon nitride in a wet atmosphere and in a dry atmosphere (0% water vapour in the figure) for 100 h are given in Fig. 1. Each data point is the average of oxidation of eight to ten specimens. The error bars represent the probable error ranges. The weight gained on oxidation in a wet atmosphere were very close to one another and although the scatter of these data was fairly large compared with those in the dry atmosphere, the mean values clearly indicated the effect of water vapour on oxidation of silicon nitride and an increasing tendency to gain weight on oxidation was found on increasing the water vapour content from 10 to 40 vol % in the atmosphere.

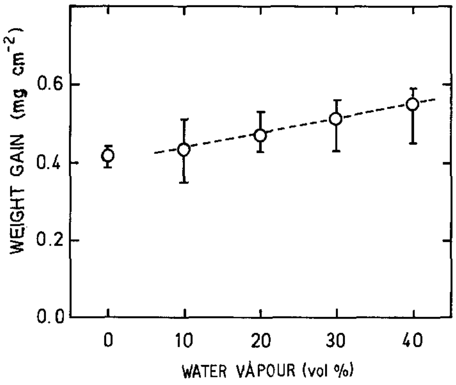


Figure 1 Weight gain on oxidation (1300° C, dry and wet atmospheres of 10 to 40 vol % H_2O).

The weight gained on oxidation in a dry atmosphere showed a slightly smaller value than that in a wet atmosphere of 10 vol % H_2O, but the difference between them was extremely small and this result was similar to the conclusions on the oxidation rates in dry air (250 p.p.m. H_2O) and in wet air (approximately 1.5% H_2O) obtained by Mayer and Riley [22]. The effect of water vapour on the oxidation of silicon nitride is not as strong as that of silicon carbide [23].

The results of this study also showed that the dispersion of weight gained on oxidation in the wet tests was large compared with that in the dry tests. One of the main reasons for this dispersion was considered to be the uneven and rugged oxide layer formed in the wet atmosphere. Fig. 2 shows the remarkable difference in surface roughness of the oxide layers obtained in dry and wet atmospheres. A more detailed discussion on the relation between the oxidation process and the surface roughness is given in Section 3.3.

The dotted line in Fig. 1 is drawn substantially through the mean values as a guide for a first approximation of the weight gained on oxidation of the specimens in four wet tests.

3.2. Kinetic measurements

To examine the oxidation kinetics of silicon nitride, the specimens were oxidized for times up to 360 h at 1300° C in a wet atmosphere with 20 vol % water vapour and in a dry atmosphere. The results are shown in Figs 3 and 4.

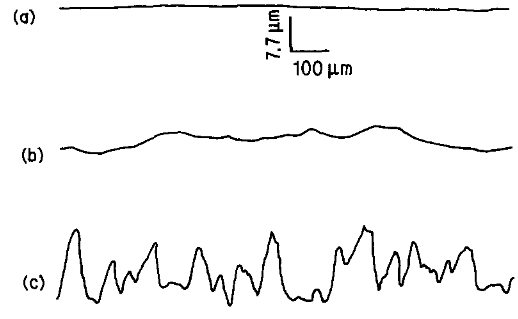


Figure 2 Surface roughness of the oxide layer formed in dry and wet atmospheres: (a) before oxidation, (b) 1300° C, 100 h in a dry atmosphere, (c) 1300° C, 100 h in a wet atmosphere of 40 vol % H_2O.

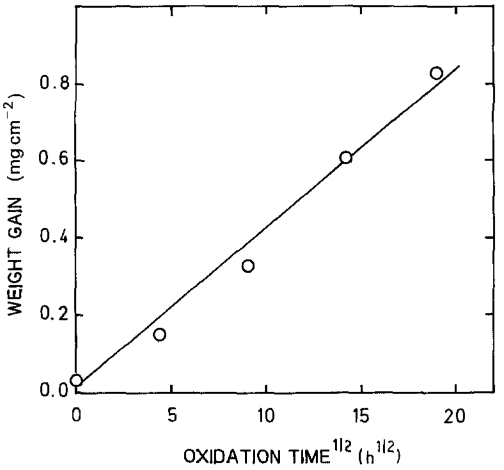


Figure 3 Parabolic plot of oxidation (1300° C, wet atmosphere of 20 vol % H_2O).

For both oxidations, the weight gain–time relation approximated the classical parabolic behaviour, implying that the diffusion of oxidants through the oxide was rate-determined.

A small but definite difference existed between dry and wet atmosphere oxidation, and the water vapour in the atmosphere accelerated oxidation of silicon nitride, as the results of wet oxidation of 10 to 40 vol % H_2O showed compared to the dry oxidation.

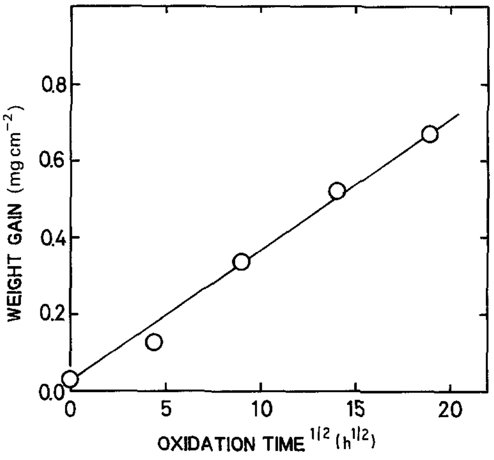


Figure 4 Parabolic plot of oxidation (1300° C, dry atmosphere).

3.3. Characterization of oxidation products

Oxidation effects on the microstructure were observed and analysed by optical microscopy, SEM, EPMA, and XRD. The surfaces of the samples oxidized at 1300° C for 100 h in a wet atmosphere of 10 to 40 vol % H_2O are shown in Fig. 5. The surface roughness became coarser with increasing water vapour content and this was reflected in the crystal growth of $Y_2O_3 \cdot 2SiO_2$ on the oxide surface. This surface roughness change was consistent with results of surface

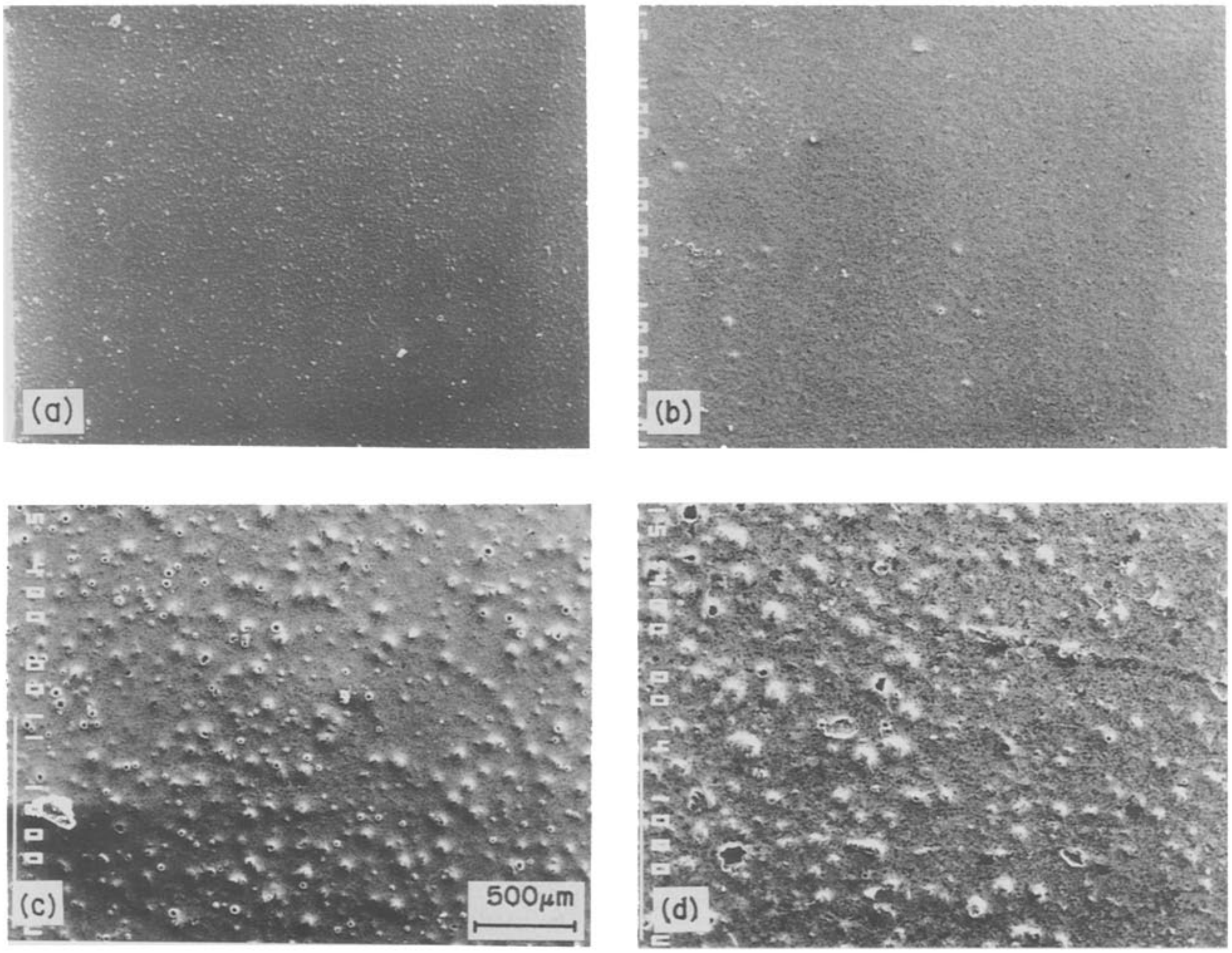


Figure 5 Scanning electron micrographs of an oxidized surface in a wet atmosphere (1300° C, 100 h, same magnifications). (a) 10, (b) 20, (c) 30, (d) 40 vol % H_2O.

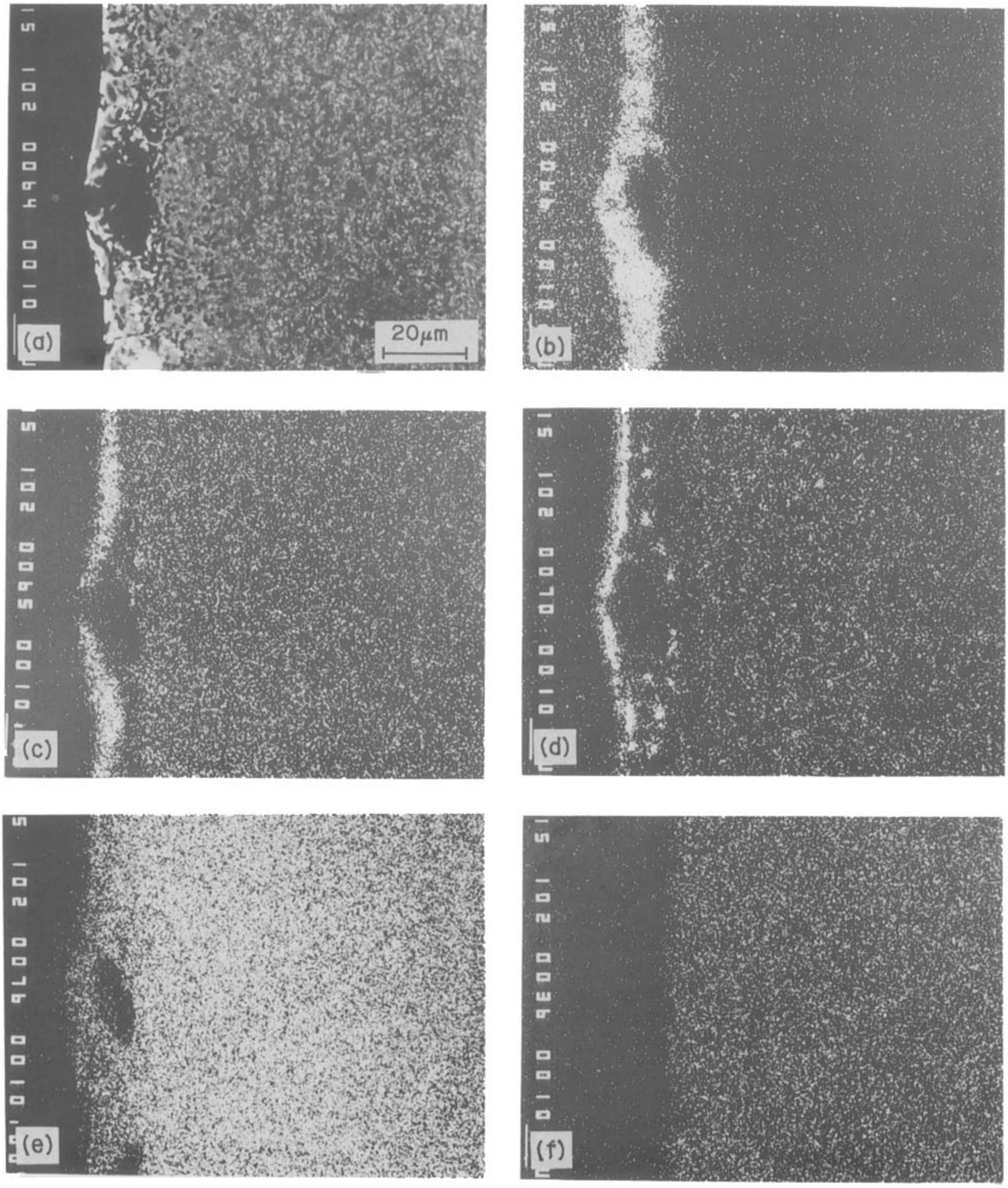
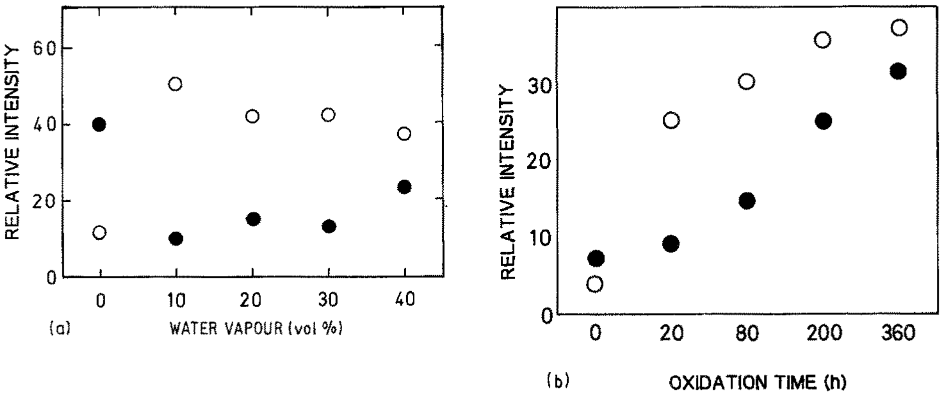


Figure 6 Scanning electron micrograph and elemental maps of the cross-section (1300° C, 100 h, 40 vol % H_2O, same magnifications). (a) Micrograph, (b) oxygen, (c) aluminium, (d) yttrium, (e) silicon, (f) nitrogen.

roughness measurement by the contact profile method (Fig. 8).

The microstructures of oxide layer were considerably porous and contained many bubbles, blowholes, cracks and distinct $Y_2O_3 \cdot 2SiO_2$ crystals. However, cristobalite was not clear in the scanning electron micrograph and it was very difficult to differentiate the amorphous silica or silicate glass from cristobalite. This is because the contrast of each electron image of the phases corresponds to the chemical composition (mean atomic number), and cristobalite and amorphous silica or silicate glass have nearly equal mean atomic numbers.

The difference in textures of the oxide layers of the four wet oxidations was slight and not well-defined. Fig. 6 shows a scanning electron micrograph and elemental distributions of oxygen, aluminium, yttrium, silicon and nitrogen of the polished cross-section of the sample oxidized in a wet atmosphere of 40 vol % H_2O for 100 h. The thickness of the oxide layer ranges from 6 to 12 μm, the layer has a porous texture and contains many bubbles and cracks. Yttrium shows the image of $Y_2O_3 \cdot 2SiO_2$ crystals in the oxide layer. Nitrogen is evenly distributed throughout the substrate and is not found in the oxide layer. Sodium, potassium, calcium and magnesium diffuse out from



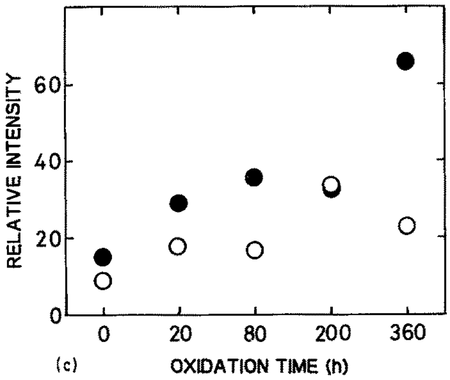


Figure 7 Relative intensity of X-ray diffraction peaks with (a) water vapour content (1300° C, 100 h); (b) oxidation time (1300° C, wet atmosphere of 20 vol % H_2O); and (c) oxidation time (1300° C, dry atmosphere). (○) cristobalite, (●) $Y_2O_3 \cdot 2SiO_2$.

the interior of the bulk into the surface and are uniformly concentrated in the oxide layer. However, aluminium is very concentrated in the outer part of the oxide layer and the inner part of the layer consists mainly of comparatively pure SiO_2, a small amount of impurity and less aluminium compared to the outer layer.

Most of the SiO_2 is probably crystallized, referring to the results of XRD, as shown in Fig. 7. Fig. 7a shows the effect of water vapour content on relative intensity of X-ray diffraction peaks in wet oxidations. The main crystals produced during oxidation were crystobalite and $Y_2O_3 \cdot 2SiO_2$. A slight decreasing tendency in the amount of cristobalite and a slight increasing tendency in the amount of $Y_2O_3 \cdot 2SiO_2$, were noticed with increasing water vapour content.

The remarkable difference between dry and wet oxidation was confirmed by the amounts of cristobalite and $Y_2O_3 \cdot 2SiO_2$. The amounts of both crystals formed were reversed in wet and dry oxidation. Fig. 7b shows the effect of oxidation time on relative intensities of X-ray diffraction peaks in wet oxidation of 20 vol % H_2O. Cristobalite and $Y_2O_3 \cdot 2SiO_2$ tended to increase with increasing oxidation time. Fig. 7c shows the effect of oxidation time on relative intensities of X-ray diffraction peaks in dry oxidation. $Y_2O_3 \cdot 2SiO_2$ increased with increasing oxidation time but cristobalite showed a complicated behaviour. It increased with time up to 200 h and then decreased toward 360 h.

From Figs 7a and b, the strong effect of water vapour on the devitrification of amorphous oxide into cristobalite was concluded. The water vapour in the atmosphere accelerated the devitrification during oxidation and the devitrification markedly increased with time.

Ogbuji [24] pointed out that the water vapour in the atmosphere accelerated the devitrification of vitreous silica and consequently promoted the SiC oxidation. Wagstaff *et al.* [25] reported that the water vapour in the atmosphere increased the crystallization rate in two ways; first, it acted as a source of oxygen, and secondly it weakened the glass structure by the formation of hydroxyls. By promoting the devitrification of

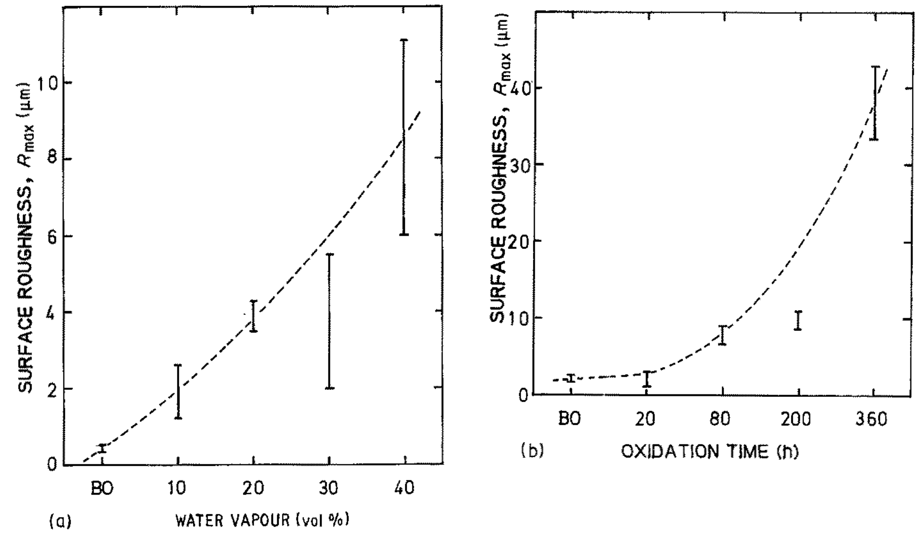


Figure 8 Surface roughness plotted against (a) water vapour content (1300° C, 100 h, BO; before oxidation), and (b) oxidation time (1300° C, wet atmosphere of 20 vol % H_2O, BO; before oxidation).

amorphous oxide by water vapour, the texture of the oxide layer became porous and the free Si_3N_4 surfaces were exposed to the atmosphere through the fissures and cracks formed by the devitrification. Then, the direct oxidation on Si_3N_4 surfaces also proceeded, in addition to the oxidation by diffusion. Therefore, it was presumed that the rate of oxidation in a wet atmosphere was promoted.

Fig. 8 shows the results of surface roughness measurement. The bars in the figures indicate the range of the dispersion of data. Fig. 8a shows the effect of water vapour content on the surface roughness and it was noted that the roughness increased with vapour content, and from Fig. 2, the surface roughness on wet oxidation showed remarkably high values compared with dry oxidation. Fig. 8b shows the effect of oxidation time on the surface roughness and it was observed that the roughness increased with time. The dotted lines in the figures were drawn as a first approximation on the surface roughness.

As mentioned in Section 3.1, the surface roughness of samples after wet oxidation was extremely uneven and rugged, thus the textures of oxide layers were also different in each sample. Therefore, it was inferred that the oxidation behaviour proceeding through these oxide layers was various and the values of weight gained by oxidation scattered widely.

3.4. Strength after oxidation

Fig. 9 shows the results of flexural strength measurement at room temperature of the silicon nitride after oxidation in a wet atmosphere. Each data point is the average of four to six breaks. Bars indicate the maximum and minimum values. Fig. 9a shows the effect of water vapour content on the flexural strength. It was evidently degraded by oxidation in a wet atmosphere but the values scattered considerably and an obvious difference was not observed among the samples oxidized in four wet atmospheres. Fig. 9b shows the effect of oxidation time on the flexural strength. The flexural strength was also apparently degraded by oxidation in a wet atmosphere but the relation between the flexural strength and oxidation time was not clear. The values were scattered extensively and the data for 80 h oxidation, especially, showed specific and high values.

According to Govila *et al.* [26], small decreases in flexural strength (less than 10%) were observed for the yttria-doped, sintered reaction-bonded silicon nitride oxidized in air at 1200 and 1400° C for 300 h, relative to room-temperature strength. Weaver and Lucek [7] measured the room-temperature flexural strength of heat-treated samples after soaking at temperatures varying from 1000 to 1300° C for 300 h found a marked decrease in strength for Si_3N_4–8% Y_2O_3 specimens soaked at $\geq$ 1100° C. Ziegler *et al.* [27] reported that the oxidation products and microcracks formed during cooling from the oxidation temperature lead to strong variations in the properties of RBSN materials; there is, for example, a strong and rather complex influence of oxidation on room-temperature strength. Strength degradation, but also an increase in strength and unaffected strength results have been observed. An unequivocal explanation cannot for the present be given for the variations in strength caused by oxidation effects. Several opposing factors might be effective, depending on the oxidation conditions and on the microstructure of the materials.

In the present work, probably the flexural strength was slightly and consecutively degraded with oxidation time. The dotted lines in the figures were drawn roughly through the dispersed values as a guide for a first approximation of the flexural strength of the specimens oxidized. In addition, no clear relation was observed between the flexural strength and surface roughness. Further experiments with more test pieces are necessary to clarify these relations.

Fig. 10 illustrates a fracture surface of the specimen oxidized at 1300° C for 100 h in a wet atmosphere of 40 vol % H_2O. The failure occurred at a course grain in the sub-surface and the mirror region is seen around the grain.

4. Conclusions

The oxidation of hot-pressed silicon nitride containing both yttria and alumina as sintering aids was performed under higher humidity environments than atmospheric conditions and also under a dry atmosphere for comparison.

On oxidation in a wet atmosphere, it was found that the weight gained increased with increasing water vapour content in the atmosphere, although the values of weight gained in the four wet conditions were very close to each other.

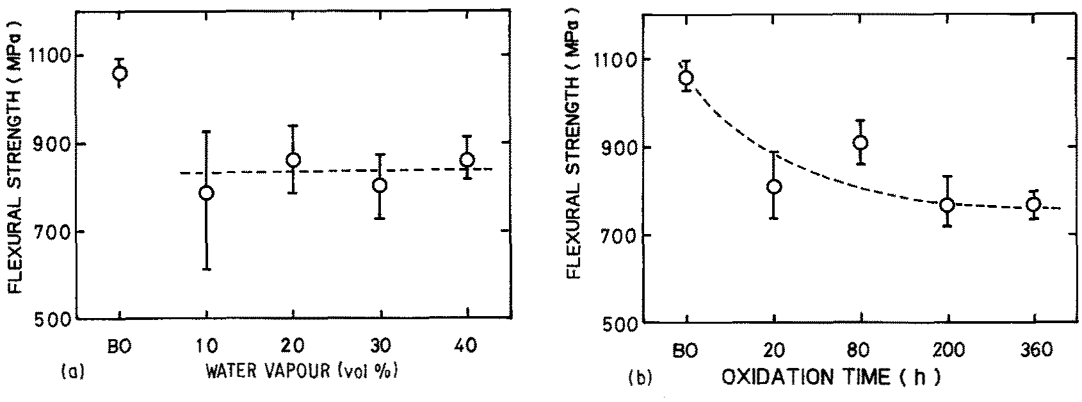


Figure 9 Flexural strength plotted against (a) water vapour content (1300° C, 100 h, BO; before oxidation), and (b) oxidation time (1300° C, 20 vol % H_2O, BO; before oxidation).

Figure 10 Scanning electron micrograph of a specimen oxidized at 1300° C for 100 h in a wet atmosphere of 40 vol % H_2O. Failure occurring at a course grain in the subsurface.

The water vapour in the atmosphere had a positive effect on the oxidation, and the values of the weight gained by oxidation were widely scattered compared to those in dry oxidation. One of the factors responsible for this dispersion was considered to be the rugged and porous oxide layer formed in the wet atmosphere.

Kinetic measurements indicated that the oxidation process was diffusion-controlled both in wet and dry atmospheres, and a small but definitive difference existed between wet and dry oxidation, reflecting the acceleration of oxidation by water vapour.

The microstructure of oxide layer was considerably porous, containing bubbles, blowholes, cracks and crystals, and no well-defined difference in texture between the four wet oxidations was found.

There was a remarkable difference in the amount of cristobalite formed during oxidation in wet and dry atmospheres. The water vapour in the atmosphere strongly accelerated the devitrification of amorphous oxide into cristobalite and the devitrification promoted porosity of oxide layer; this process was presumed to promote the rate of oxidation to a greater extent in a wet atmosphere than in a dry one. Devitrification proceeded with time.

The water vapour in the atmosphere had a strong roughening effect on the surface oxide layer grown during oxidation and the surface roughness increased with increasing water vapour content and time.

The flexural strength at room temperature was degraded by oxidation in a wet atmosphere but there was no difference between the four humidities tested. Flexural strength is presumed to be slightly degraded by wet oxidation, increasing with time.

References

1. R. W. DAVIDGE, A. G. EVANS, D. GILLING and P. R. WILYMAN, in "Special Ceramics 5", edited by P. Popper (British Ceramic Research Association, Stoke-on-Trent, 1972) p. 329.
2. A. J. KIEHLE, L. K. HEUNG, P. J. GIELISSE and T. J. ROCKETT, *J. Amer. Ceram. Soc.* **58** (1975) 17.
3. W. C. TRIPP and H. C. GRAHAM, *ibid.* **59** (1976) 399.
4. S. C. SINGHAL, *J. Mater. Sci.* **11** (1976) 500.
5. J. B. WARBURTON, J. E. ANTILL and R. W. M. HAWES, *J. Amer. Ceram. Soc.* **61** (1978) 67.
6. D. CUBICCIOTTI and K. H. LAU, *ibid.* **61** (1978) 512.
7. G. Q. WEAVER and J. W. LUCEK, *Amer. Ceram. Soc. Bull.* **57** (1978) 1131.
8. P. BARLIER and J. P. TORRE, *J. Mater. Sci.* **14** (1979) 235.
9. Y. HASEGAWA, H. TANAKA, M. TSUTSUMI and H. SUZUKI, *Yogyo-Kyokai-Shi* **88** (1980) 292.
10. Y. HASEGAWA, T. YAMANE, K. HIROTA, M. TSUTSUMI and H. SUZUKI, *ibid.* **89** (1981) 46.
11. T. SATA and K. FUJII, *ibid.* **90** (1982) 110.
12. T. E. EASLER, R. C. BRADT and R. E. TRESSLER, *J. Amer. Ceram. Soc.* **65** (1982) 317.
13. J. E. SHEEHAN, *ibid.* **65** (1982) C-111.
14. L. J. LINDBERG, D. W. RICHERSON and W. D. CARRUTHERS, *Amer. Ceram. Soc. Bull.* **61** (1982) 574.
15. G. N. BABINI, A. BELLOSI and P. VINCENZINI, *J. Mater. Sci.* **18** (1983) 231.
16. *Idem, ibid.* **19** (1984) 1029.
17. O. J. GREGORY and M. H. RICHMAN, *J. Amer. Ceram. Soc.* **67** (1984) 335.
18. D. M. MIESKOWSKI and W. A. SANDERS, *ibid.* **68** (1985) C-160.
19. R. K. GOVILA, *J. Mater. Sci.* **22** (1987) 1193.
20. R. M. HORTON, *J. Amer. Ceram. Soc.* **52** (1969) 121.
21. S. C. SINGHAL, *ibid.* **59** (1976) 81.
22. M. I. MAYER and F. L. RILEY, *J. Mater. Sci.* **13** (1978) 1319.
23. M. MAEDA, K. NAKAMURA and T. OHKUBO, *ibid.* **23** (1988) 3933.
24. L. U. OGUBUJI, *ibid.* **16** (1981) 2753.
25. F. E. WAGSTAFF, S. D. BROWN and I. B. CUTLER, *Phys. Chem. Glasses* **5** (1964) 76.
26. R. K. GOVILA, J. A. MANGELS and J. R. BAER, *J. Amer. Ceram. Soc.* **68** (1985) 413.
27. G. ZIEGLER, J. HEINRICH and G. WOTTING, *J. Mater. Sci.* **22** (1987) 3041.

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