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Oxidation resistance of silicon nitride ceramics with various additives

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Five silicon nitride ceramics with various additives were evaluated for their oxidation resistance at 1300° C in flowing dry and wet air. In a dry atmosphere, the oxidation of all types of Si_3N_4 except one proceeded in two stages with different reaction rates nearly following the parabolic law. In a wet atmosphere, all types showed a linear relationship between weight gain by oxidation and water varpour content. The water vapour in the atmosphere slightly accelerated the oxidation. The influence of oxidation on room-temperature strength was complex, but there was no observed distinguishable difference of the effect on the flexural strength between dry and wet oxidation.

1. Introduction

Silicon nitride is a candidate material for high-temperature structural applications because of its excellent high-temperature strength and high resistance to oxidation. However, for long-term operation or under severe atmospheric conditions, the oxidation behaviour is of major importance. The oxidation of silicon nitride ceramics has been studied extensively [1–6], but most results are with respect to short-term oxidation under a dry atmosphere.

The study of the oxidation behaviour under a wet atmosphere or for long times is of considerable engineering interest. Generally, the oxidation behaviour of non-oxide ceramics is quite complex and the reproducibility of oxidation data is invariably poor, because of many factors influencing the oxidation [7]. Proper evaluation of oxidation resistance requires specifying and controlling atmospheric test conditions. Comparison of oxidation data should only be done if the test conditions are specified.

In the present paper, the oxidation resistance of five types of silicon nitride ceramics were evaluated and the oxidation effect on the room-temperature flexural strength was demonstrated in dry and wet atmospheres.

2. Experimental procedure

Five types of silicon nitride ceramics were investigated and their properties are listed in Table I. 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 JIS R1601 [8]. The samples were cleaned ultrasonically in acetone and alcohol.

The oxidation was performed in two different atmospheres, dry and wet. The oxidation in the dry atmosphere was done in a flowing dry air after passage through molecular sieve cylinders.

The oxidation in the wet atmosphere was performed under flowing humid air containing 1, 3, 5, 10, 20, 30 and 40 vol % water vapour and under a still atmosphere without air flow. The humid air was produced by a humidifier with water evaporator, dry air producer and gas mixer. The dew point of the humidified air was measured by a hygrometer at the position just in front of the air inlet to the oxidation test furnace and monitored by a recorder.

The oxidations were carried out in an electric tubular furnace at 1300° C and the air flow rate was

TABLE I Properties of silicon nitride ceramics

	Specimen				
	S	M	H	N	Y
Sintering aid	$Sc_2O_3 + Cr_2O_3$	$MgO + Al_2O_3$	$Y_2O_3 + Al_2O_3$	$Y_2O_3 + Al_2O_3$	$Y_2O_3 + Al_2O_3$
Sintering process	HP	Pressureless	HP	HP	Pressureless
Chemical analysis					
(wt %): Al	0.15	1.84	0.98	1.29	1.18
Mg	0.003	0.73	0.012	0.013	0.007
Cr	0.20				
Sc	1.40				
Y			2.92	3.82	3.26
Bulk density	3.167	3.124	3.125	3.213	3.210
Porosity (%)	0.157	0.260	0.306	0.114	0.303

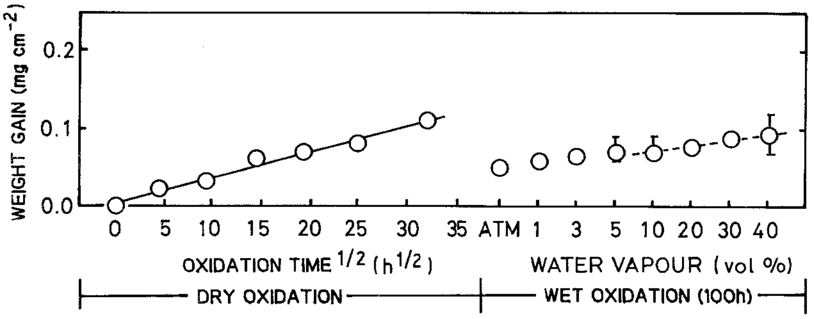

Figure 1 Weight gain on oxidation in dry and wet atmospheres at 1300°C. ATM, oxidation in the atmosphere (specimen S).

1600 ml min^{-1} in both atmospheres. The oxidation time in the dry atmosphere was up to 1000 h and in the wet atmosphere was fixed at 100 h.

All five types of specimen were arranged together in a row on a pressureless-sintered silicon carbide setter and loaded in the centre of the furnace. The oxidation resistance was evaluated by measuring the weight change before and after oxidation with a semi-micro balance weighing to 0.01 mg.

The strength distributions were determined on a four-point loading fixture with an outer span of 3.00 cm with an inner span of 1.00 cm (one-third-point loading). All flexural strength testings were carried out at 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

The relationship between weight gain by oxidation and oxidation time in dry and wet atmospheres of five types of silicon nitride ceramics is illustrated in Figs 1 to 5 in which the weight gains are plotted on a (time)$^{1/2}$ axis. Four to six pieces were tested for each type of specimen and the bars in the figure indicate the maximum and minimum values. In the case of the circle without bar, all values of that test fell in the range of the circle size.

3.1.1. Dry atmosphere

The oxidation reaction in a dry atmosphere of all five kinds of specimen followed approximately the parabolic rate law. However, except for specimen S shown in Fig. 1, the parabolic plots of all of the other four kinds of specimen, shown in Figs 2 to 5, exhibited a break midway up to 1000 h oxidation.

The oxidation of specimen S apparently seemed to proceed in one stage, but the absolute values of the weight gains by oxidation were very small. Therefore, the oxidation data of specimen S are presumed to be relatively uncertain, compared to the data on the other specimens with larger weight gains by oxidation. If specimens with a larger surface area than those used in this experiment were tested, much more accurate oxidation data could be obtained, which might exhibit the two-stage oxidation.

According to Davidge *et al.* [9], the oxidation of reaction-bonded silicon nitride (containing 20% open porosity) occurs in two well-defined stages; at internal (stage I) and external (stage II) surfaces. They stated that the oxidation could occur at both surfaces provided that the internal pores were not completely filled or that a continuous film was not formed at the surface. Because the internal surface area is greater than the external area, the oxidation in stage I is much more rapid than in stage II.

The specimens tested in the present work were dense bodies having a low porosity (~0.306%). Therefore, the role of open porosity, which is important in RBSN materials (~20%), is presumed to be a secondary factor in this oxidation test.

Tripp and Graham [10] proposed several possible explanations for a change in reaction mechanism. Therefore, the break observed on the parabolic plot could have been correlated with these phenomena.

Specimen S with scandia as additive, showed an excellent oxidation resistance as reported by Dodsworth and Thompson [11]. Specimens H, N and Y contain the same sintering additives, yttria and alumina, in different amounts. Specimens H and N, which are both produced by hot-pressing, give superior products to specimen Y which was made by pressureless sintering and showed better oxidation resistance than specimen Y [12].

According to Wu *et al.* [13], hot-pressed Si_3N_4 materials with MgO additive showed larger weight gain by oxidation than that with Y_2O_3 additive in the same amount (wt %) of additive as the former. In this

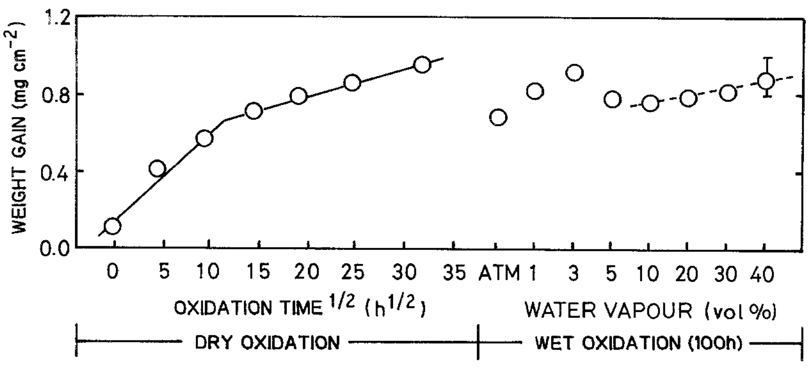

Figure 2 Weight gain on oxidation in dry and wet atmospheres at 1300°C. ATM, oxidation in the atmosphere (specimen M).

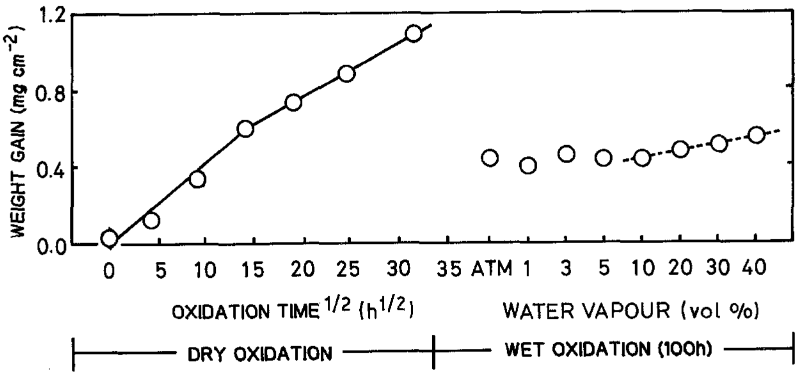

Figure 3 Weight gain on oxidation in dry and wet atmospheres at 1300° C. ATM, oxidation in the atmosphere (specimen H).

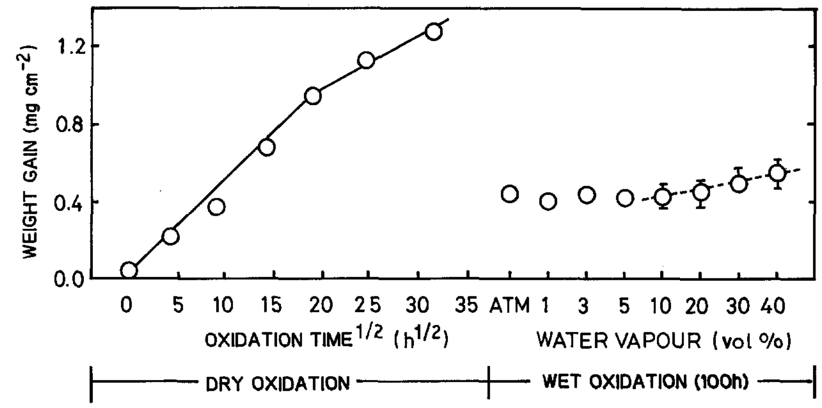

Figure 4 Weight gain on oxidation in dry and wet atmospheres at 1300° C. ATM, oxidation in the atmosphere (specimen N).

experiment, specimen M with MgO and Al_2O_3 additives showed less weight gain by oxidation than specimens H, N and Y, which have all Y_2O_3 and Al_2O_3 additives. This is probably due to the small amount of MgO additive in specimen M.

3.1.2. Wet atmosphere

The right-hand sides of Figs 1 to 5 give the relationship between weight gain by oxidation and water vapour content in the wet atmosphere. The dotted lines in the figures are roughly drawn as a guide for a first approximation of the weight gain of oxidized specimens.

It is seen that all five kinds of specimen have a linear relationship between weight gain by oxidation and water vapour content with but few exceptions. This result clarified that the water vapour in the atmosphere accelerated somewhat the oxidation of silicon nitride compared with that in a dry atmosphere [14, 15], although the effect is not stronger than for silicon carbide ceramics [16].

Specimen M showed a higher weight gain by oxidation in the atmosphere with 5 vol % and less water vapour than with the water vapour above 10 vol %, under which atmosphere the relationship between the weight gain by oxidation and water vapour content was erratic.

In specimen Y, the weight gain by oxidation in the wet atmosphere with 5 vol % water vapour only, deviated from the linear relation and showed slightly higher values, contrary to the other values under all other wet conditions. The reason for this peculiar phenomenon is not clear at present.

3.2. Flexural strength

Figs 6 to 10 show the relationships between flexural strength and oxidation time in a dry atmosphere and between flexural strength and water vapour content in a wet atmosphere of specimens S, M, H, N and Y.

Four to six specimens were fractured for each test; bars in the figures indicate the maximum and minimum values and dotted lines are roughly drawn

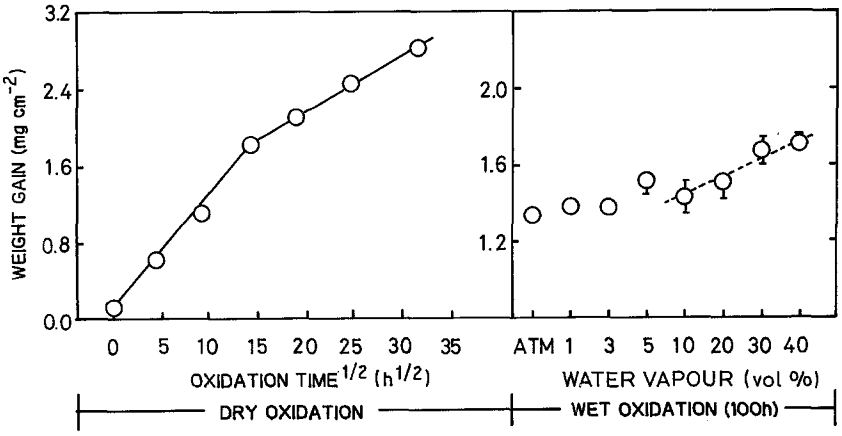

Figure 5 Weight gain on oxidation in dry and wet atmosphere at 1300° C. ATM, oxidation in the atmosphere (specimen Y).

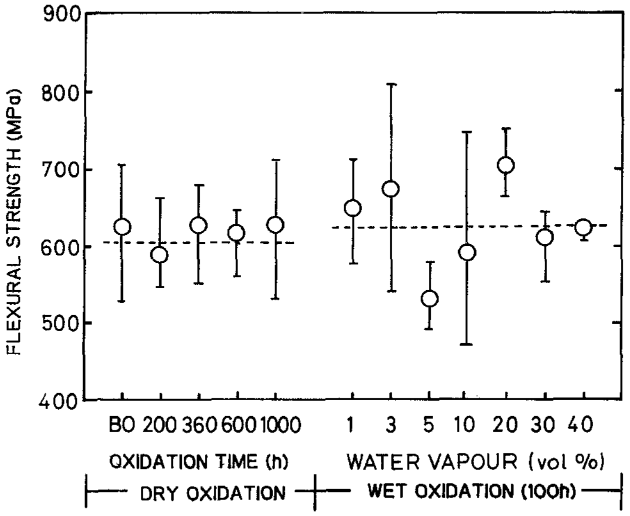

Figure 6 Relationship between flexural strength and oxidation time in a dry atmosphere and between flexural strength and water vapour content in a wet atmosphere. BO, before oxidation (specimen S).

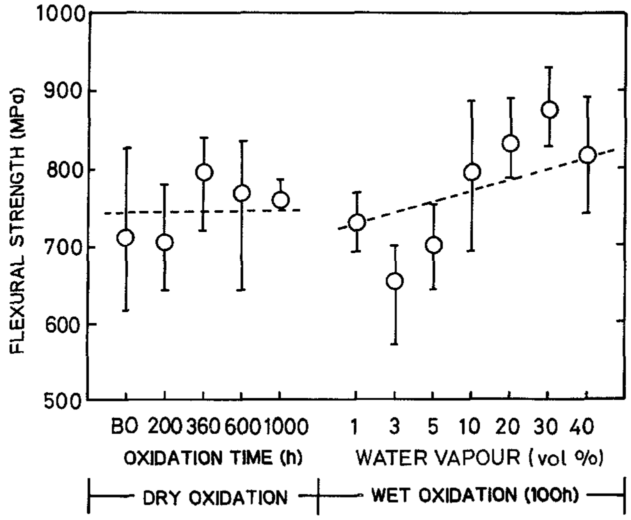

Figure 8 Relationship between flexural strength and oxidation time in a dry atmosphere and between flexural strength and water vapour content in a wet atmosphere. BO, before oxidation (specimen H).

through the lower limits as a guide for a first approximation of the strength of oxidized specimens.

3.2.1. After dry oxidation

Wu *et al.* [13] have studied the oxidation behaviour and strength degradation, due to long-term high-temperature exposure in air (100 h), of Si_3N_4 with MgO, ZrO_2 or Y_2O_3, as densification additives. They found that the strength was significantly reduced (30% to 60%) for almost all compositions except for the body with 8 wt % Y_2O_3.

Easler *et al.* [17] studied the effects of oxidation on the strength distributions of sintered Si_3N_4 with yttria and alumina as sintering additives, and hot-pressed Si_3N_4 with 8% yttria additive, and for both Si_3N_4 materials, the oxidation at 1370° C resulted in an initial strengthening after a short period ($\frac{1}{2}$ h) of oxidation, followed by strength decreases after further oxidation for up to 50 h. They commented that the initial increase is presumably due to oxidative blunting of the crack tips, whereas prolonged oxidation results in the generation of new flaw populations containing more severe flaws.

Govila *et al.* [18] observed small decreases (less than 10%) in flexural strength at room-temperature for the yttria-doped sintered reaction-bonded silicon nitride, oxidized in air at 1200 and 1400° C for 300 h.

Lange *et al.* [19] reported that the slight strengthening of MgO-doped hot-pressed Si_3N_4 was obtained at room-temperature after the oxidation at 1400° C for 322 h and this strengthening may be attributed to the compressive stresses developed by the volume increase and compositional gradient produced during oxidation.

In the present work, specimen S and H did not show noticeable degradation in strength for up to 1000 h, but specimen N showed a remarkable degradation (~ 30%). Specimens M and Y showed a consecutive degradation with oxidation time.

Although, at present, unequivocal explanations cannot be given for these degradations in strength caused by the oxidation effects, but as mentioned by Wu *et al.* [13] and Lange *et al.* [19], the strength changes were presumably related to the formation of pits and cracks in an oxidized surface, and the volume and compositional changes of the body developed during oxidation [20]. Ziegler *et al.* [6] stated that there have been very different types of behaviour reported

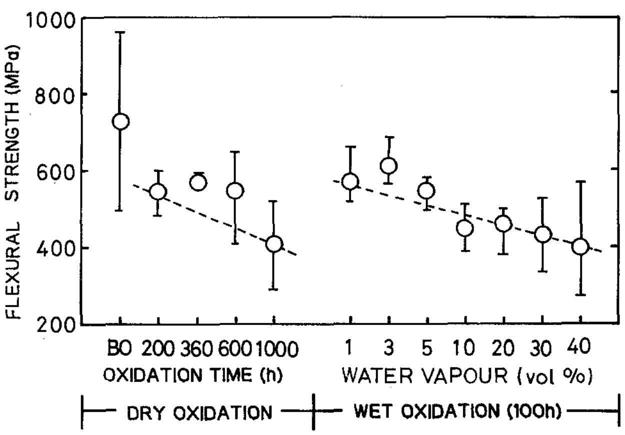

Figure 7 Relationship between flexural strength and oxidation time in a dry atmosphere and between flexural strength and water vapour content in a wet atmosphere. BO, before oxidation (specimen M).

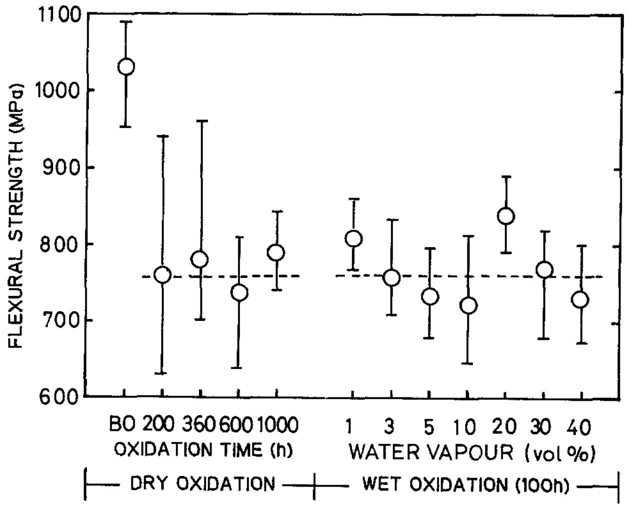

Figure 9 Relationship between flexural strength and oxidation time in a dry atmosphere and between flexural strength and water vapour content in a wet atmosphere. BO, before oxidation (specimen N).

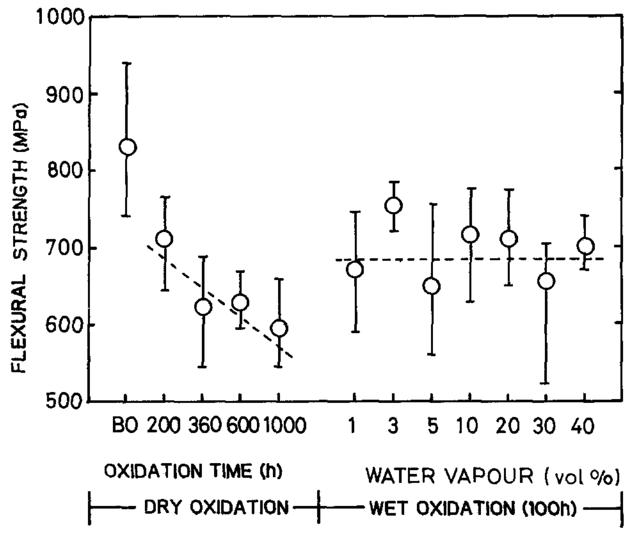

Figure 10 Relationship between flexural strength and oxidation time in a dry atmosphere and between flexural strength and water vapour content in a wet atmosphere. BO, before oxidation (specimen Y).

of the influence of oxidation on room-temperature strength, depending on the experimental conditions.

3.2.2. After wet oxidation

Specimens S, N and Y showed no obvious change in strength after wet oxidation and no considerable difference of the effect on the water vapour content in the atmosphere, except for some deviated values (5 and 20 vol % wet test of specimen S, 1 and 20 vol % wet test of specimen N and 3 vol % wet test of specimen Y) which are considered to be within the variations of experimental data.

Specimen M showed consecutive losses in strength, and specimen H showed a consecutive strengthening with an increase in the amount of water vapour. The degradation in strength of specimen M is presumably related to coarsening of the surface oxide layer and the textural and compositional change of the body based on the microstructural observations of the cross-sectioned specimens. The strength of specimen H after the wet oxidation in low contents of water vapour ($\lesssim 10$ vol %) showed comparative values with the strength of specimen N, but the strength of specimen H had a tendency to increase with increasing amount of water vapour in the wet test atmosphere.

The reason for this large difference in the effect of wet oxidation on flexural strength between specimens H and N, which contain the same additives, is not clear at present, but it might be related to the difference in the amount of additives.

4. Conclusions

Five kinds of silicon nitride ceramics with various additives were tested for their oxidation resistance at 1300° C in dry and wet atmospheres.

1. The oxidation of all kinds, except one, proceed in two stages with different reaction rates nearly following the parabolic rate law in the dry atmosphere.

2. All five kinds had an approximately linear relationship between weight gain by oxidation and water vapour content, except for a few exceptions in the wet atmosphere.

3. Water vapour in the atmosphere accelerated the oxidation of silicon nitride, but the effect is not strong compared to silicon carbide ceramics.

4. The influence of oxidation on room-temperature strength was rather complex.

In dry oxidation, silicon nitride with Sc_2O_3 and Cr_2O_3(S) and silicon nitride with Y_2O_3 and Al_2O_3(H) were unaffected, silicon nitride with Y_2O_3 and Al_2O_3(N) was degraded, silicon nitride with MgO and Al_2O_3(M) and silicon nitride with Y_2O_3 and Al_2O_3(Y) were consecutively degraded in strength.

In wet oxidation, silicon nitride H increased, S, N and Y were unaffected, and M was degraded in strength. However, there was no distinguishable difference of the effect on the flexural strength between dry and wet oxidation.

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