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Oxidation of silicon carbide in a wet atmosphere

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The effects of water vapour on oxidation of pressureless-sintered silicon carbide containing alumina as a densifying aid were studied in a 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 times up to 360 h. The weight gain on oxidation showed an increasing tendency with increasing water vapour content. Water vapour in the atmosphere strongly influenced oxidation and accelerated the reaction. Oxidation in a wet atmosphere proceeded in a diffusion-controlled manner, in the same process as that for the dry atmosphere. No remarkable differences were noticed in the microstructure of the oxide layer and the surface roughness between the samples oxidized under the four wet conditions, but the surface roughness increased with increasing oxidation time. Water vapour evidently accelerated the devitrification of amorphous silica and promoted oxidation. Oxidation in a wet atmosphere (10 to 40 vol % H_2O for 100 h and 20 vol % H_2O up to 360 h) had a slight degrading effect on the flexural strength. The microstructure or surface roughness of the oxide layer formed during oxidation presumably had very little effect on the room-temperature strength.

1. Introduction

Silicon carbide is a promising material for high-temperature structure components because of its excellent high-temperature strength and creep resistance. The utilization of this material instead of the traditional metallic components offers many advantages; increased efficiencies owing to higher-temperature operation, lightening of bodies and making use of rich materials in natural resources.

One of the principal factors affecting their performance is the oxidation behaviour; extensive thermal oxidation could lead to failure of the components. Although a considerable amount of work has been performed to investigate the kinetics of oxidation of SiC [1–10], few data are available of the effects of water vapour on the oxidation [11–14], uncertainties exist and no satisfactory explanations have been given.

Most of the data show that water vapour accelerates the oxidation of SiC. Jorgensen *et al.* [14] reported that water vapour played a strong role in the crystallization of amorphous silica and accelerated SiC oxidation by promoting devitrification. Suzuki [15] also studied the role of steam in the oxidation of silicon carbide; he found that, in general, water vapour was an oxidizing agent for silicon carbide. The rate of oxidation was accelerated when water vapour was added to oxygen, and Suzuki proposed that possibly water vapour was accelerating the diffusion of oxygen, carbon monoxide, or carbon dioxide through the layer of SiO_2 or that water vapour promoting the transition of amorphous silica to cristobalite might account for the accelerated rate.

Wagstaff and Richard [16] assumed that water vapour enhanced the crystallization of silica glass as catalyst. Ogbuji [17] reported that water vapour accelerated the devitrification of vitreous silica and, consequently, promoted SiC oxidation. Schiroky's [18] explanation of the accelerating effect of water vapour on SiC oxidation was that possibly the introduction of hydroxyl groups into the silica network produced a less dense silica film which allowed for faster diffusion of oxidizing species and/or reaction products, i.e. CO.

The present study was undertaken to provide data on the oxidation of SiC under environments of higher humidity than atmospheric conditions and to elucidate the effect of water vapour on the oxidation.

2. Experimental procedure

Oxidation kinetics were determined in wet and dry atmospheres at 1300° C of pressureless sintered silicon carbide containing alumina as densifying aid.

2.1. Materials

Specimens were rectangular bars of dimensions 3 mm × 4 mm × 40 mm. The specimen surfaces were ground to less 0.8 μm of R_{max} 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 [19]. The samples were cleaned ultrasonically in acetone and alcohol. Bulk density

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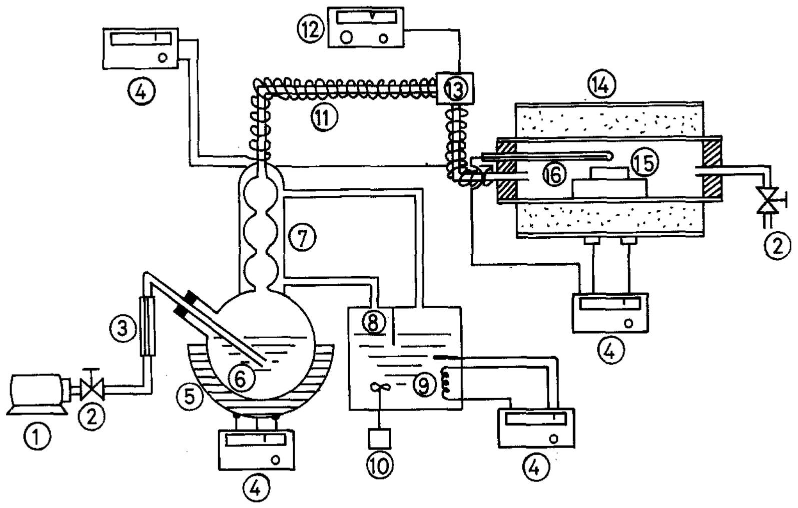


Figure 1 Diagram of wet-testing apparatus. 1, air pump; 2, needle valve; 3, flow meter; 4, temperature controller; 5, mantle heater; 6, evaporator; 7, condenser; 8, water pump; 9, water bath; 10, stirrer; 11, ribbon heater; 12, hygrometer; 13, hygrometer sensor; 14, electric furnace; 15, specimen; 16, thermocouple.

was measured by the displacement method and ranged from 3.18 to 3.25 g cm^{-3}. The amounts of the major components of the SiC specimen, as determined by chemical analysis, are shown in Table I.

2.2. Oxidation

The oxidation in a wet atmosphere was performed using an electric tube furnace with a water vapour producer and hygrometer, shown in Fig. 1. The humidity of the air bubbled into the water in the evaporator by the air-pump was controlled by the electric power supply to the evaporator heater and adjusting the circulating water temperature of the water bath for the condenser.

The dew point of the wet air was measured by a hygrometer at a position just in front of the air inlet to the oxidation test furnace and 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 oxidation time was 100 h for all the experiments except for the kinetic measurements.

The kinetic measurements were carried out in two different atmospheres; one was in a dry atmosphere and the other was in a wet atmosphere with 20 vol % water vapour. Oxidation times were up to 360 h (15 days) and the air flow rate was 800 ml min^{-1}. In the dry test, oxidation was performed in flowing air after passage through a drying train of silica gel and dispersed phosphorous pentoxide drying towers. The specimens were placed on a high-purity alumina sample holder and loaded in the centre of furnace.

2.3. Measurements

The specimens were characterized by measuring the weight change before and after the oxidation with a semi-micro balance weighing to 0.01 mg, 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 was 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 (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.

TABLE I Chemical analysis (wt %)

Al	B	Free C	Total C
2.44	0.001	<0.05	27.0

3. Results and discussion

3.1. Oxidation in a wet atmosphere

The weight gains produced by oxidation of silicon carbide in wet and dry atmospheres (0% water vapour in the figure) for 100 h are given in Fig. 2. Each data point is the average of oxidation of eight to ten specimens. The error bars represent the probable error ranges. A slight increasing tendency for weight gain on oxidation was found on increasing the water vapour content from 20 to 40 vol % in the atmosphere. In the wet test with 10 vol % water vapour, the weight gain deviated from this tendency and resulted in higher values than that of the wet test of 40 vol % water vapour. The dotted line in the Fig. 2 is drawn approximately through the mean values as a guide for first approximation of the weight gain by oxidation of the specimens oxidized in four wet tests.

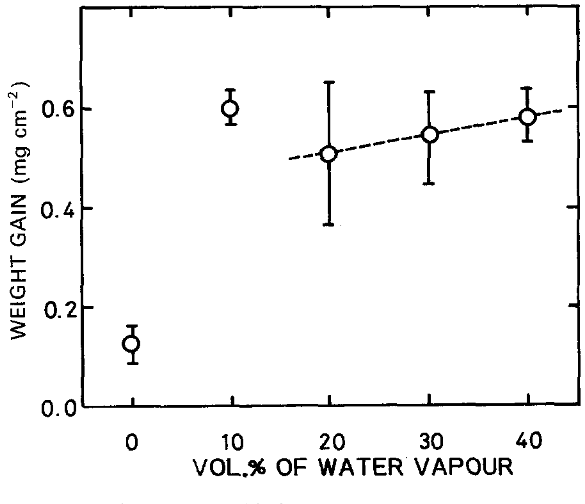


Figure 2 Weight gain on oxidation.

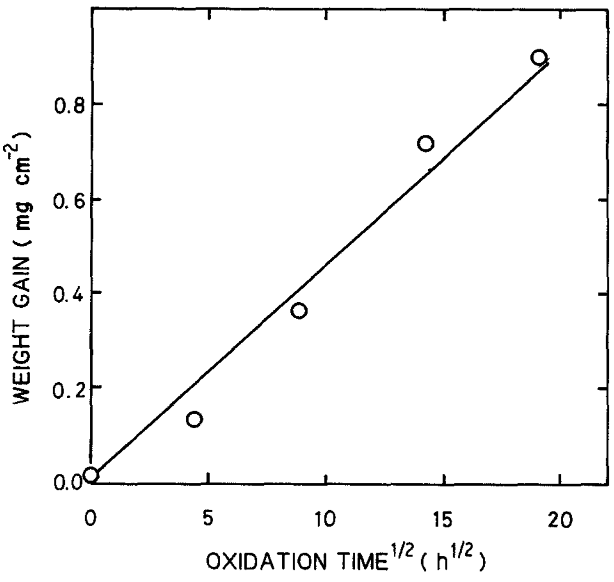


Figure 3 Parabolic plot of oxidation (1300° C, 20 vol % H_2O).

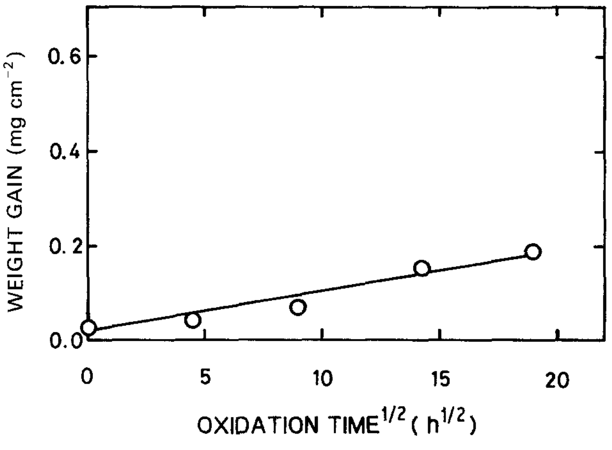


Figure 4 Parabolic plot of oxidation (1300° C, dry atmosphere).

Considering the dispersion of measurement values, it might be difficult to find a significant difference in the weight gains on oxidation among the results of four wet tests, only from these data. However, in an other investigation of the effects of water vapour on oxidation [20], results almost identical to those in this study were obtained for a silicon carbide specimen of the same kind. Another remarkable result was that the maximum weight gain on oxidation of each wet test were almost the same (0.63 to 0.65 mg cm^{-2}) in the wet tests under all four conditions. The reasons for these two specific phenomena are not clear at present, but may well be related to the disturbance [21] of the atmosphere occurring during oxidation in the test furnace.

Barlier *et al.* [22] and Gregory *et al.* [23] mentioned that a gaseous boundary layer was formed during oxidation of the reaction-bonded silicon nitride. This comment also suggests the complexity and inhomogeneity of the atmosphere during oxidation.

3.2. Kinetic measurements

To examine the oxidation kinetics of silicon carbide, the specimens were oxidized for times up to 360 h at 1300° C in the wet atmosphere with 20 vol % water vapour, and in a dry atmosphere. The results are shown in Figs 3 and 4. For both oxidations, the weight gain against time relation approximated classical parabolic behaviour, implying that the diffusion of oxidant through the oxide is rate-determining.

A definite difference existed between dry and wet atmospheres, and the tests showed that water vapour influenced strongly the oxidation of silicon carbide and it accelerated the reaction.

3.3. Oxide layer characterization

Oxidation effects on the microstructure were observed and analysed by optical microscopy, SEM, EPMA and XRD. The surfaces of samples oxidized at 1300° C for 100 h in a wet atmosphere of 20 and 40 vol % H_2O are shown in Figs 5a and b. Both appear identical.

Fig. 6a shows a scanning electron micrograph and Figs 6b, to e are the elemental maps of oxygen, silicon, potassium and aluminium, respectively, of polished cross-sections of the sample oxidized at 1300° C for 100 h in a wet atmosphere of 30 vol % H_2O.

SEM and EPMA studies showed that oxide layers were generally porous and contained many bubbles, blowholes and channels, and potassium diffused outwards into the surface from the interior and aluminium dispersed uniformly in the oxide layer. It was confirmed by EPMA that most of other impurities also in a sample were concentrated in the oxide layer.

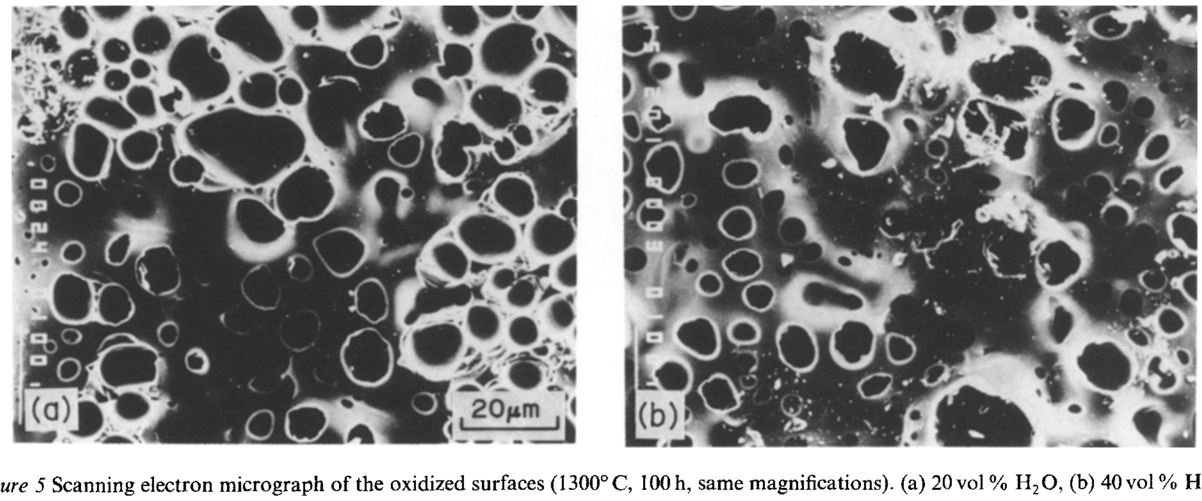


Figure 5 Scanning electron micrograph of the oxidized surfaces (1300° C, 100 h, same magnifications). (a) 20 vol % H_2O, (b) 40 vol % H_2O.

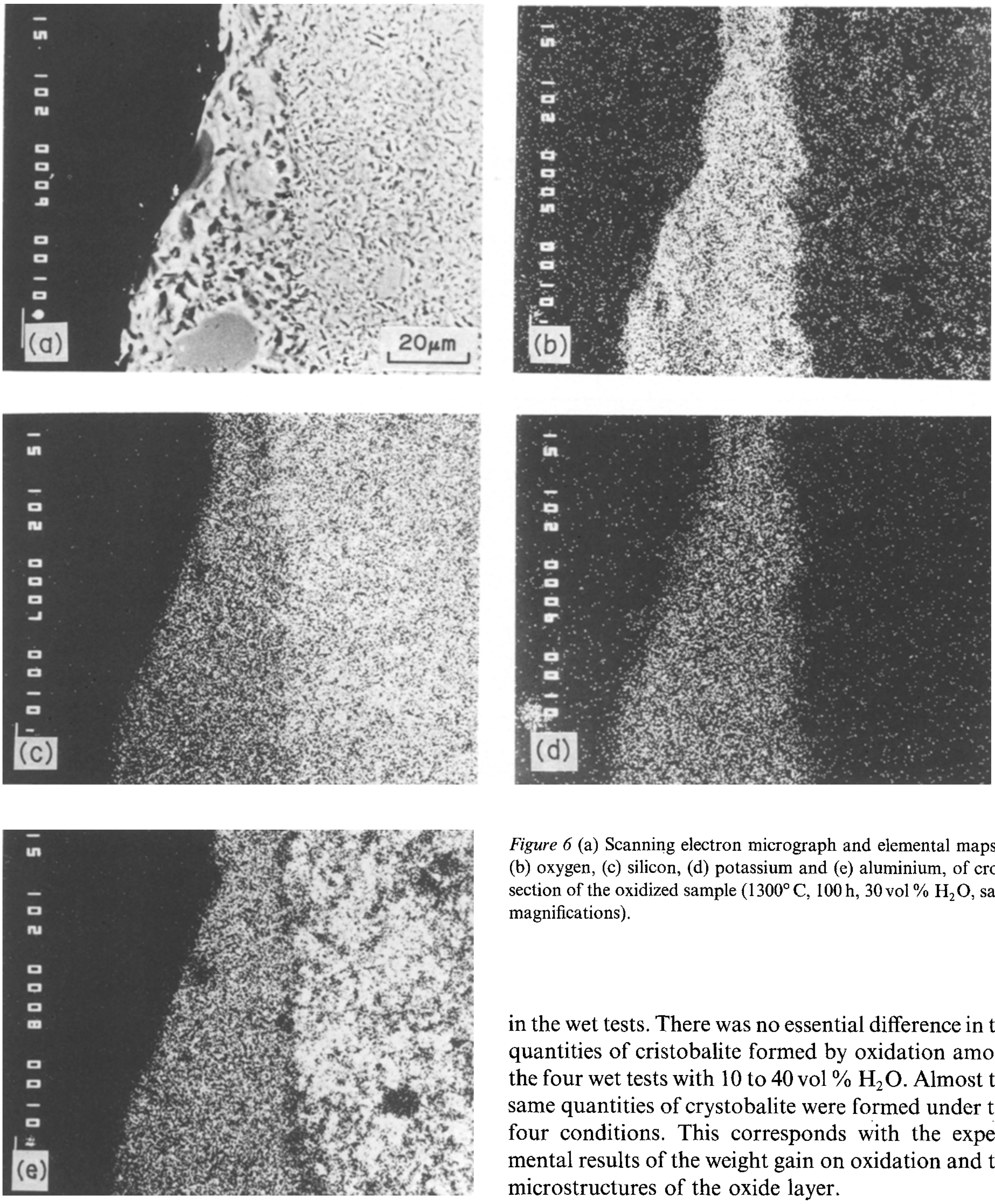


Figure 6 (a) Scanning electron micrograph and elemental maps of (b) oxygen, (c) silicon, (d) potassium and (e) aluminium, of cross-section of the oxidized sample (1300° C, 100 h, 30 vol % H_2O, same magnifications).

The gaseous reaction product of oxidation may initially diffuse to the surface, but with increased oxide layer the thickness nucleates gas bubbles near the oxidation front. At intermediate layer thickness, these bubbles expand and burst, resulting in uneven surface topography and oxide layers full of blowholes of various sizes.

Generally, no remarkable differences were noticed between the microstructures of oxide layers of the samples oxidized under the four different wet conditions.

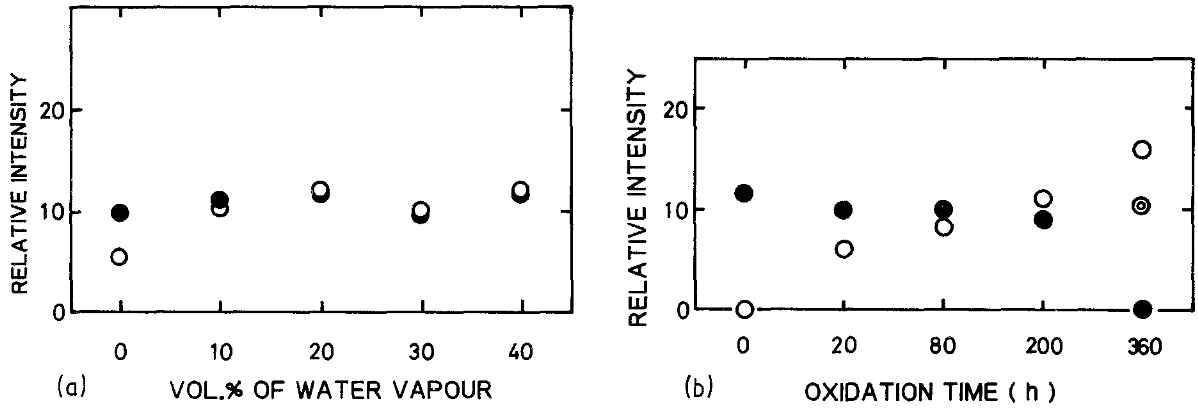
From the scanning electron micrograph of Fig. 6a, the crystals and glass phase which constitute the oxide layer, are not clear but cristobalite and corundum were detected by XRD. Fig. 7 shows the results of XRD. Fig. 7a shows the effect of water vapour content on the relative intensity of X-ray diffraction peaks in the wet tests. There was no essential difference in the quantities of cristobalite formed by oxidation among the four wet tests with 10 to 40 vol % H_2O. Almost the same quantities of crystobalite were formed under the four conditions. This corresponds with the experimental results of the weight gain on oxidation and the microstructures of the oxide layer.

Corundum existed from the beginning as sintering aid in the specimens.

Fig. 7b shows the effect of oxidation time on the relative intensity of X-ray diffraction peaks in wet tests of 20 vol % H_2O. Cristobalite had a tendency to increase with increasing oxidation time and after 360 h oxidation, corundum disappeared from the oxidized surface and mullite crystals, which were newly formed by consuming cristobalite as one of the components, appeared.

Fig. 7c shows the effect of oxidation time on the relative intensity of X-ray diffraction peaks in the dry test; cristobalite again increased with increasing oxidation time.

Jorgensen *et al.* [14] and Ogbuji [17] pointed out that water vapour in the atmosphere accelerated the devitrification of vitreous silica and, consequently, promoted the SiC oxidation. This behaviour was also observed in this study. The quantity of cristobalite



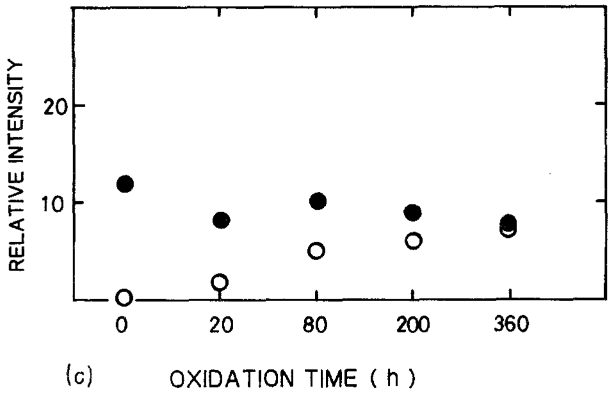


Figure 7 Relative intensities of X-ray diffraction peaks (a) against water vapour content (1300° C, 100 h), (○) cristobalite, (●) corundum; and against oxidation time (b) (1300° C, 20 vol % H_2O), (○) cristobalite, (●) corundum, (◎) mullite; (c) (1300° C, dry atmosphere) (○) cristobalite, (●) corundum.

formed in the oxidation by dry tests (Fig. 7c) was less than that obtained in wet tests (Figs 7a and b).

Fig. 8 shows the results of surface roughness measurement. Fig. 8a shows the effect of water vapour content and Fig. 8b shows the effect of oxidation time on surface roughness. There was no distinct difference in the surface roughness formed during oxidation among the four wet tests of 10 to 40 vol % H_2O.

Compared with the surface roughness obtained in the dry test, that obtained in the wet test showed an extremely high value, and on wet testing the surface roughness increased with increasing in oxidation time, as shown in Fig. 8b. The dotted lines in the figures were drawn as a first approximation of the surface roughness of the specimens oxidized in a wet atmosphere.

Fig. 9 is the result of flexural strength measurement. 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 and Fig. 9b shows the effect of oxidation time on flexural strength. The flexural strength was slightly degraded by oxidation in a wet atmosphere (10 to 40 vol % H_2O for 100 h and up to 360 h in 20 vol % H_2O). The dotted lines in the figures were drawn approximately through the dispersed values as a guide for first approximation of the flexural strength of the specimens oxidized. The curves remained virtually the same; the strengths showing no marked degradation. In comparison with the experimental results of Fig. 8b, no relationship between the flexural strength and surface roughness could be deduced from the results of Fig. 9b.

Easler *et al.* [24] indicated that the sintered SiC exhibited little change in the flexural strength after oxidation at 1370° C for 50 h.

Within the experimental limitations of this study, it was assumed that the structure of the oxide layer formed on the sample surface had very little effect on the mechanical properties of sintered silicon carbide. The present data, however, are insufficient to quantitatively substantiate these conclusions.

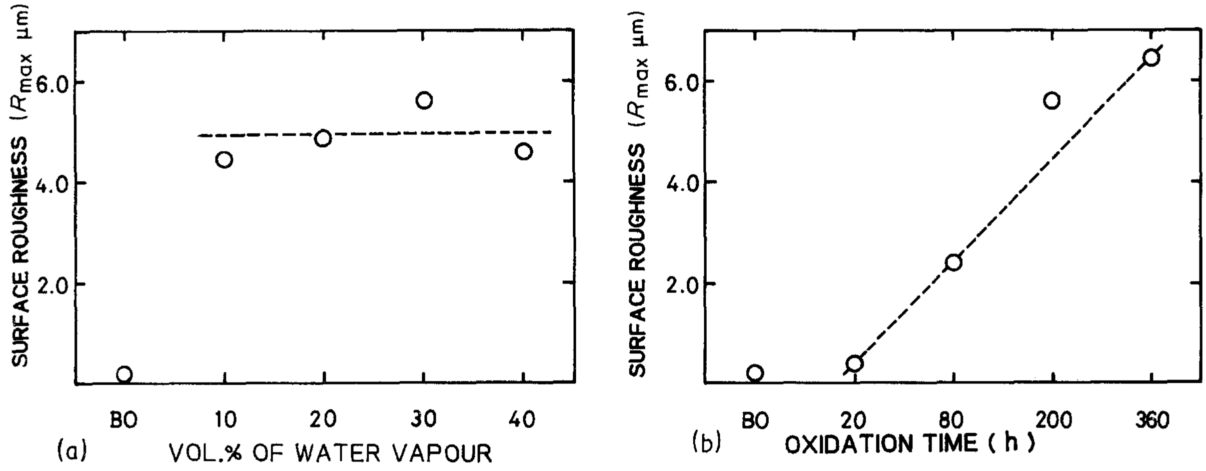


Figure 8 Plots of surface roughness (a) against water vapour content (1300° C, 100 h, BO; before oxidation), and (b) against oxidation time (1300° C, 20 vol % H_2O, BO; before oxidation).

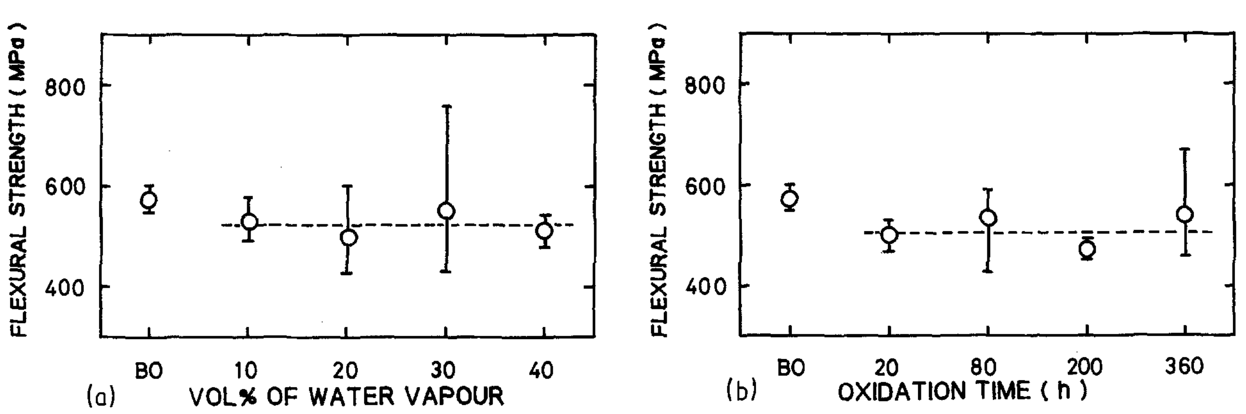


Figure 9 Plots of flexural strength (a) against water vapour content (1300° C, 100 h, BO; before oxidation), and (b) against oxidation time (1300° C, 20 vol % H_2O, BO; before oxidation).

4. Conclusions

Pressureless-sintered silicon carbide was oxidized under higher humid environments than atmospheric conditions and also under a dry atmosphere for comparison. The following points summarize the major findings of this report.

1. The weight gain by oxidation increased with increasing in water vapour content in the atmosphere except for the wet test with 10 vol % H_2O.

2. A definite difference existed between dry and wet tests which showed that water vapour strongly influenced the oxidation of silicon carbide and accelerated the reaction.

3. From the oxidation kinetics experiments, it was found that both oxidation in dry and wet atmospheres approximated the classical parabolic behaviour and the reaction was diffusion-controlled.

4. Generally, no remarkable differences were noticed in the microstructure of the oxide layers and the surface roughness formed during oxidation between the samples tested under the four wet conditions for 100 h, but the surface roughness increased with the increasing oxidation time.

5. Water vapour accelerated the devitrification of amorphous silica and promoted oxidation of SiC.

6. The flexural strength of silicon carbide was slightly degraded by oxidation in a wet atmosphere (10 to 40 vol % H_2O for 100 h and up to 360 h in 20 vol % H_2O).

7. No definitive evidence of a correlation between the flexural strength and the microstructure or the surface roughness of oxide layer was noted, indicating that they had presumably very little effect on the flexural strength at room temperature of sintered silicon carbide.

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