# Oxidation of Silicon Carbide in Oxygen and in Water Vapour at 1500 °C

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The oxidation of silicon carbide with various mixtures of O_2, H_2O and N_2 or Ar was studied by passage of the reactant gas through a bed of 20 mesh silicon carbide grains at 1500 °C and analysis of the exit gas. Oxidation in H_2O+N_2 gives SiO_2, CO_2, CO and H_2 as products, with no detectable amounts of volatile silicon species formed. The oxidation rate in H_2O+N_2 (or Ar) appears almost independent of time, whereas the rate in O_2+N_2 follows the parabolic law and is much lower than in H_2O+N_2. The rate in H_2O+O_2 is equal to that in H_2O+N_2. Mechanisms for the processes are discussed and compared to the analogous oxidation processes for silicon.

Silicon carbide has found widespread applications in refractory materials for use in oxidizing atmospheres. The service life at elevated temperatures is mainly limited by the gradual oxidation to silica. This forms the background for a number of investigations concerning the rate of oxidation of silicon carbide. This field has recently been reviewed by Schlichting,[1] hence a general literature survey is not given here.

Oxidation of silicon carbide in oxygen (or air) takes place according to the straightforward eqn. (1).

$$SiC(s) + 2O_2(g) = SiO_2(s) + CO_2(g) \qquad (1)$$
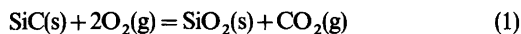
The silica is formed as a coherent layer on the surface of the carbide and slows down the rate of further oxidation.

Silicon carbide will also oxidize in water vapour. Lea[2] probably was the first to note a surprisingly high rate of oxidation in a mixture of oxygen and water vapour. Since that time, oxidation in mixed atmospheres as well as in water vapour alone has been studied by several workers (see Schlichting's review for references). The high oxidation rates in water vapour have been substantiated, but it appears that the chemical reaction between water vapour and silicon carbide has not been explicitly stated.

In the absence of oxygen, the oxidation in water vapour would be expected to take place according to eqn. (2).

$$SiC(s) + 3H_2O(g) = SiO_2(s) + CO(g) + 3H_2(g) \qquad (2)$$
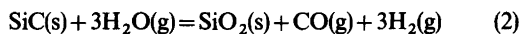
The carbon monoxide will to some extent react with the excess water vapour, eqn. (3).

$$CO(g) + H_2O(g) = CO_2(g) + H_2(g) \qquad (3)$$
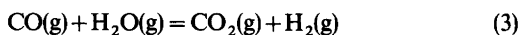
The equilibrium constant of the latter reaction at 1500 °C is about 0.2, but the equilibrium is strongly shifted towards the right with decreasing temperature.

The aim of the present work was to see whether eqn. (2) is a correct representation of the reaction in water vapour, and to compare rates in water vapour and in oxygen.

EXPERIMENTAL

Oxidation of silicon carbide commonly has been studied on powder samples, placed in a boat or crucible with the oxidizing atmosphere flowing past the surface of the powder bed. As has been emphasized by Ebi, Fitzer and Hüttinger,[3] reaction rate constants derived from such experiments may be seriously in error on the low side because the
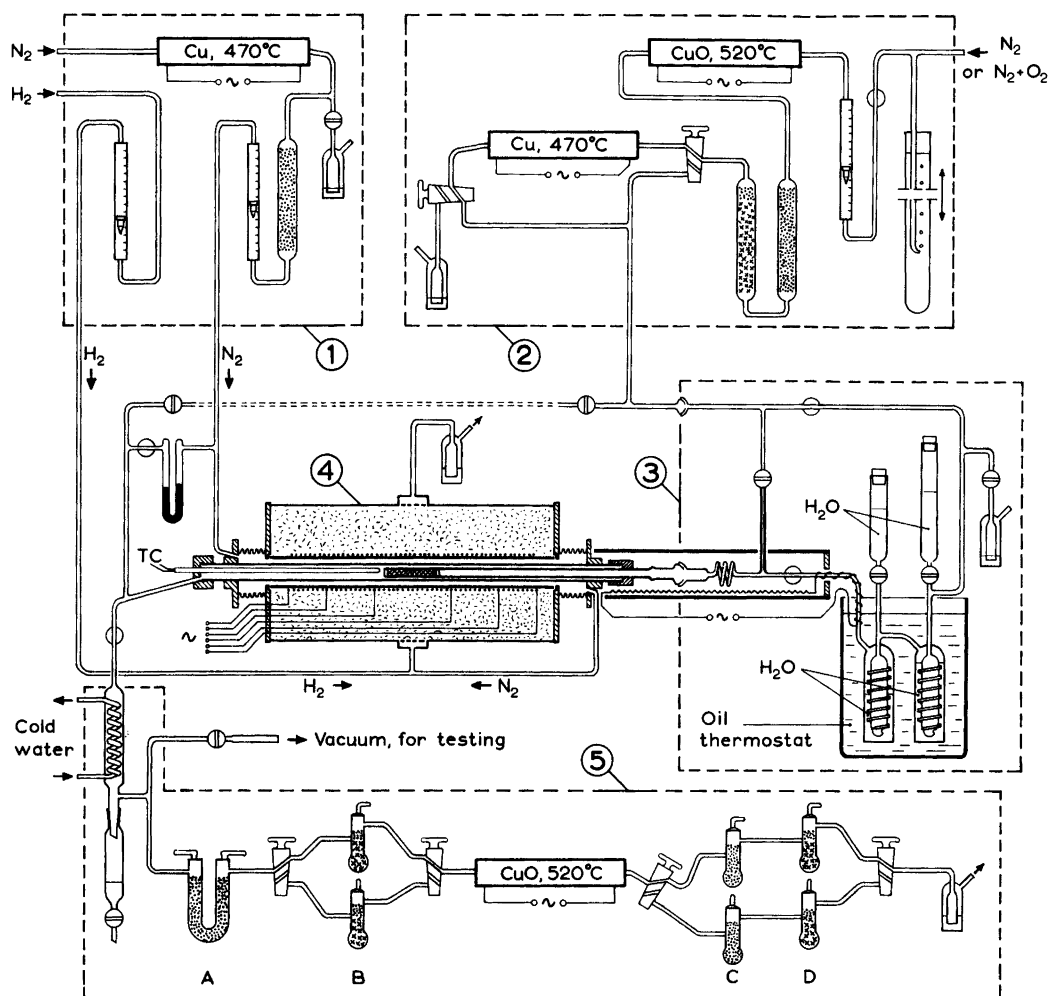
Fig. 1. Apparatus for oxidation of silicon carbide in oxygen and/or water vapor. (1) Purification train for protection gas to furnace. (2) Purification train for reaction gas. (3) Water-saturating section (heater and temperature control not shown). (4) Molybdenum-wound furnace, with silicon carbide charge shown cross-hatched. (5) Section for drying and analysis of exit gas. Tubes A and C are charged with drying agent (Dehydrite), B and D with carbon dioxide absorbent (Ascarite).

oxidant gas has to diffuse through the interspace between grains, countercurrent to the gaseous reaction products. In the present study this difficulty was avoided by placing the SiC sample as a fixed bed filling the entire cross section of the reaction tube, so that the reactant gas was forced through the bed. The silicon carbide used was of grain size No. 20 (U.S. Abrasive Standard), light green, transparent grains.* Treatment with hydrofluoric acid indicated

0.15 % or less of surface silica, and the grains were used as received. A charge weight of 13.50 g was used in each run.

The apparatus is shown in Fig. 1, which is largely selfexplanatory. The reaction tube, about 10 mm I. D., refractory porcelain * was placed concentrically in an intermediate alumina tube, which is turn was placed concentrically in the alumina tube carrying the molybdenum heater windings of the furnace.

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*SIKA I brand, from Arendal Smelteverk, Eydehavn, Norway.

* Pythagoras brand from W. Haldenwanger, Germany.

Nitrogen, or alternatively argon, was used as carrier gas for the water vapour. For most of the experiments the thermostat for the water saturation was kept at 81.7 ± 0.1 °C, thus giving $P_{H_2O} = 0.5$ atm. For the oxygen runs, a mixture of oxygen and nitrogen in the ratio 1:1 was used to allow direct comparison with the results from water vapour oxidation. The gas flow rate measured at room temperature was kept at 3 ml/s for the nitrogen − oxygen mixture, 1.5 ml/s for the carrier gas in the water vapour runs, to give the same flow rate in the furnace in both cases. Gas transfer lines were made of glass throughout.

Prior to each run, the apparatus was tested for leaks by evacuation and detection of pressure rise in the closed system. Heating was then started with a constant flow of pure nitrogen (or argon) through the furnace. The rate of heating was not allowed to exceed about 250 °C per hour to avoid cracking of the alumina tubes,[4] the heating-up period thus totalled 6 to 7 h. When 1500 °C was reached, the gas was changed to the desired reaction gas mixture, simultaneously turning the stopcocks joining the

absorbtion vessels A to D, cf. Fig. 1. This moment was taken as zero time. The temperature of the furnace was kept at 1500 ± 2 °C by means of a Pt/90Pt10Rh thermocouple coupled to a potentiometric controller. The short-time temperature cycling was about 0.1 °C as read from a second thermocouple placed next to the reaction tube.

The molybdenum windings of the furnace were protected from oxidation by a mixture of nitrogen and hydrogen. In the first few experiments this gas flowed through the interspace between the two alumina tubes of the furnace. Blank runs then showed that significant amounts of hydrogen went through the intermediate tube and into the reactant (or inert) gas. Alumina tubes, originally tested and found vacuum tight, develop leaks progressively when used in a hydrogen-containing atmosphere at 1500 °C. The difficulty was remedied by rearranging the protection gas flow, with pure nitrogen between the two alumina tubes as shown in Fig. 1. Subsequent blank runs showed no hydrogen in the exit gas.
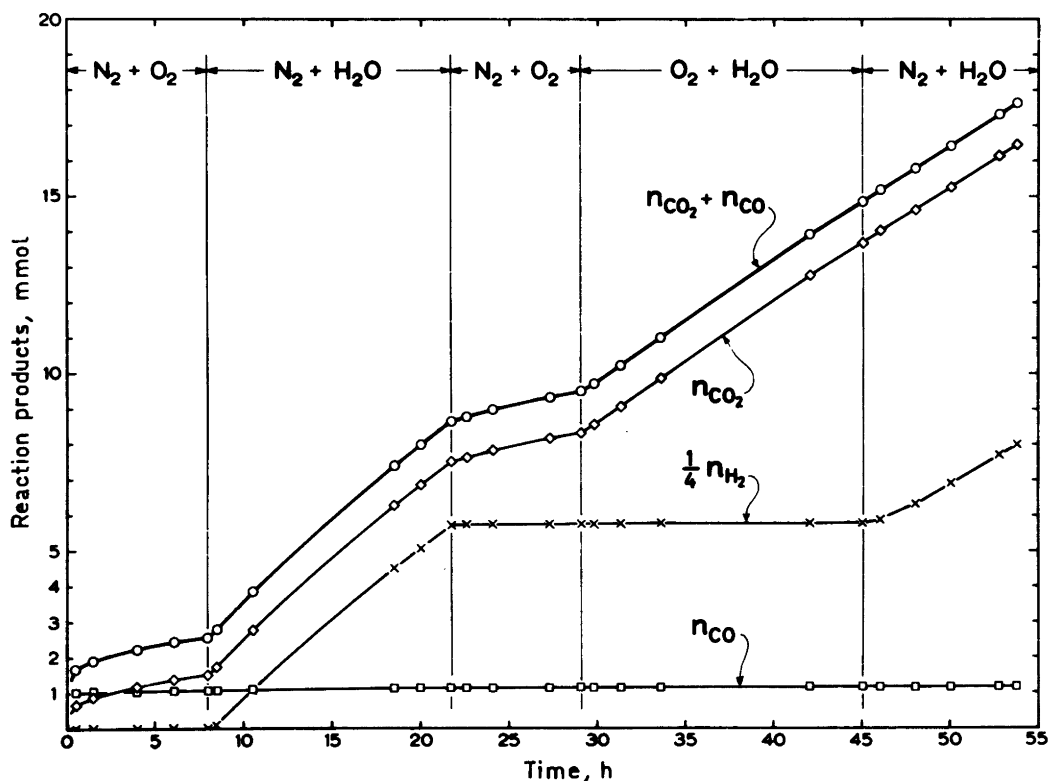

Fig. 2. Reactions products, in mmol, as functions of time, for run No. 7. Curve for $n_{CO} + n_{CO_2}$ corresponds to curve on Fig. 3 for same run.

RESULTS

In the work of Lea[2] he indicated that the enhanced rate of oxidation in water vapour might be caused in part by increased volatility of silica in steam. In order to check this hypothesis, the first four runs with water vapour were made with a platinum condenser tube fitted to the exit end of the reaction tube, extending into the cold end of the furnace. No significant weight change of this tube was detected, however, and it is concluded that volatile silicon species do not play a significant part in the reaction.

If eqn. (2) is appropriate for the reaction with water vapour, and eqn. (3) is also taken into account, the number of mol of gaseous reaction products should obey the relation (4). The amounts in mol of CO_2, H_2 and CO, as determined from the weight

$$n_{H_2} = 4n_{CO_2} + 3\,n_{CO} \qquad (4)$$

gains of absorption tubes B, C and D of Fig. 1, were found to obey this relation. This is demonstrated in Fig. 2 where the accumulated amounts of each of the species are plotted against time for run No. 7. It is seen also that in the very first part of the run, carbon monoxide is formed in preference to carbon dioxide, which means that the reaction during the first few minutes is sufficiently rapid to deplete the gas of its oxygen content. In the remainder of the run, the CO formed by reaction (2) is almost completely oxidized to CO_2 by the excess water vapour before leaving the furnace, consistent with the increase in equilibrium constant of reaction (3) with decreasing temperature.
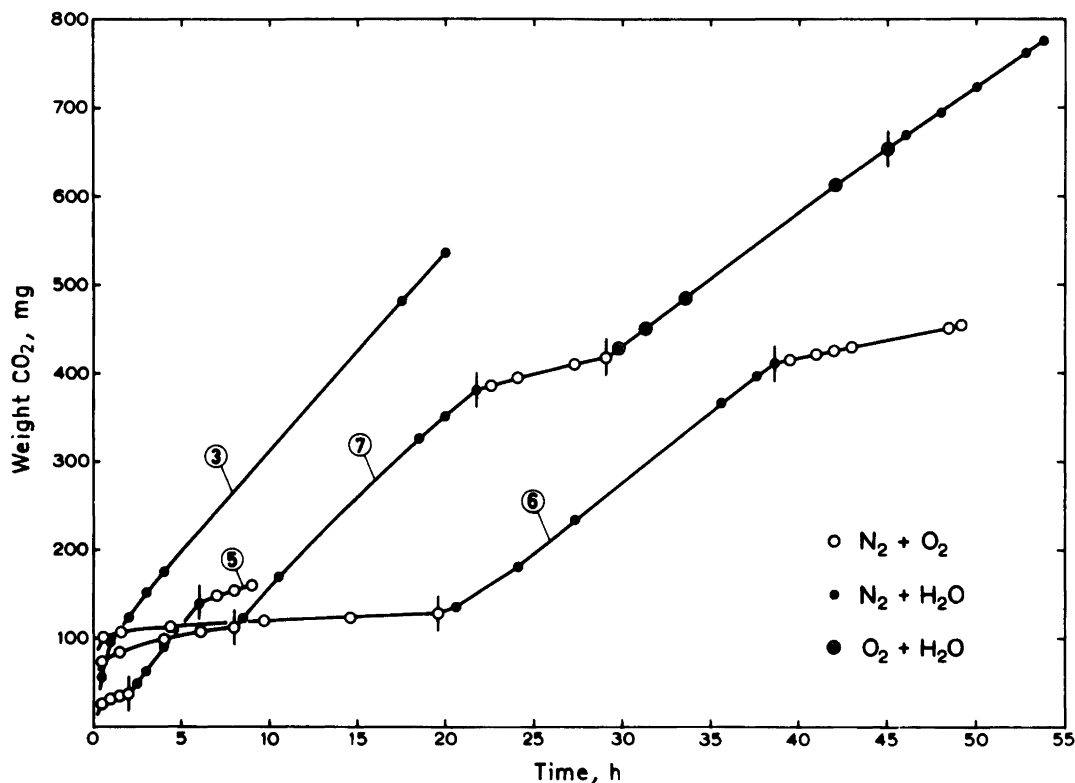

Fig. 3. Oxidation of silicon carbide at 1500 °C, total weight of carbon dioxide as a function of time, for runs Nos. 3, 5, 6 and 7. Nitrogen used as inert gas during heating-up. Oxidation in oxygen and/or water vapor as indicated on figure, partial pressures of reactant gases 0.5 atm. Vertical bars indicate point of time for change of gas.
Charge in all runs: 13.50 g silicon carbide grain No. 20. Each 100 mg carbon dioxide correspond to 0.674 % of charge reacted, and to a silica film thickness of approximately 1.3 μm.

The amounts of CO_2, H_2 and CO were determined during all of the runs, and were found to agree with eqn. (4) within a few percent. For the consideration of the oxidation rates it is sufficient to report here the sum of weight gains in absorption tubes B and D, *i.e.*, the mass of CO_2 collected. This is done graphically in Figs. 3 and 4. (Runs 1, 2, 4 and 11 were blank runs, the observations from blank run 11 only being included in the graphs.)

Considering first Fig. 3, at least five distinct features of the results will be pointed out. Firstly, at the very start of the run the oxidation proceeds with a much higher rate than consistent with the subsequent parabolic behaviour. Secondly, after the rapid initial phase was over, the oxidation in O_2 $+N_2$ was found to proceed according to the parabolic law whereas the rate of oxidation in H_2O $+N_2$ was found to be nearly independent of time. Thirdly, when oxidation was initially carried out with oxygen and the gas was then changed to water vapour, the oxidation rate increased by almost a

factor of ten. Fourthly, when the sample which had been oxidized with water vapour again was subjected to dry O_2+N_2, the oxidation rate decreased (by a factor of about three) but remained higher than the previous rate in oxygen, in spite of the thickness of silica added in the meantime. Fifthly, from run 7 it appears that in the presence of water vapour the rate of oxidation was the same regardless of whether the permanent gas was nitrogen or oxygen.

All runs in Fig. 3 were done with a slow stream of pure nitrogen during heating-up. In order to check whether the observed rapid initial oxidation was caused by some interaction between silicon carbide and nitrogen during heating-up, another series of runs was made with argon during the heating. The results are plotted in Fig. 4. It is seen by comparison with Fig. 3 that no significant differences were observed when argon was substituted for nitrogen. The rapid initial oxidation still was observed (and still was of a not very reproducible magnitude).
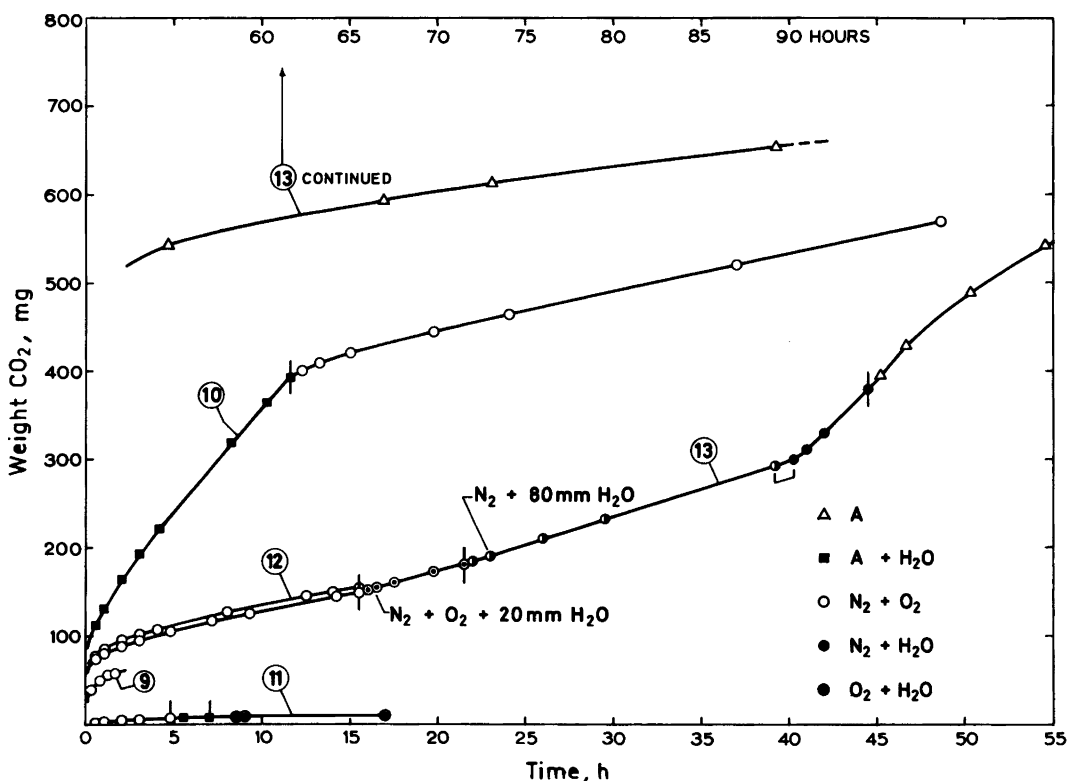

Fig. 4. Result plotted as in Fig. 3, for runs Nos. 9 – 13, with argon as inert gas during heating-up. Temperature and charge as given for Fig. 3. No. 11 is a blank run with a previously unused reaction tube.

In run No. 13, after an initial oxidation in O_2 + N_2, several gas mixtures with varying partial pressures of water vapour were admitted in a somewhat haphazard way, and finally the gas was changed to pure argon. As a result the apparent oxidation rate, measured by the amount collected CO_2, *increased*, later to decrease somewhat but remaining at a high value through the remaining 45 h of the run. This is believed to be caused by reaction (5). In principle the equilibrium of reaction (5) should

$$2SiO_2(s) + SiC(s) = 3SiO(g) + CO(g) \qquad (5)$$
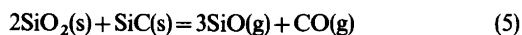
be established regardless of the atmosphere, but in the presence of an oxidizing gas the reaction is effectively stopped by the reoxidation of SiO. The formation of SiO in run No. 13 was evidenced by a generous deposit of brownish condensate towards the exit end of the furnace after the end of the run. X-Ray diffraction analysis of this condensate showed silicon metal plus weaker lines of α-cristobalite, formed by disproportionation of SiO on cooling.

Another evidence for SiO-formation was that within ten hours after changing to argon, both thermocouples broke. It is well known that even minor amounts of silicon monoxide are detrimental to platinum alloys due to formation of platinum silicide, and it has been observed in this laboratory that silicon monoxide may diffuse through dense-sintered alumina protection tubes at temperatures around 1500 °C.

DISCUSSION

Assuming that the parabolic oxidation rate of silicon carbide in dry oxygen is controlled by the diffusion of oxygen through the silica layer, one would expect that this rate can be correlated with the rate of oxidation of silicon metal under the same conditions. That this is actually so was shown nearly twenty years ago,[5] based on the experimental evidence avilable at that time. One would then also expect similarities between the oxidation of SiC and Si in water vapour. Thus in the discussion to follow, some reference will be given to studies of the oxidation of Si as well as of SiC.

The high initial rate. It is known that silicon carbide evaporates with an excess of silicon in the vapour phase, free carbon being formed on the solid surface. It might be assumed that such evaporation took place to some extent during heat-up in a flowing inert gas, and that the subsequent rapid evolution of

CO or CO_2 in an oxidizing gas was caused by oxidation of the free carbon. There has been some disagreement as to the magnitude of the vapour pressures of silicon carbide,[6] but calculations show that at the temperature and flow velocity of the present work, no more than a few tenths of a mg of free carbon could be formed during heat-up. This cannot then explain the observed initial rate. On the other hand, heating in a flowing inert gas constitutes an efficient process for removal of surface silica from the silicon carbide through reaction (5). Hence when oxidizing gas is admitted, the reaction at first takes place on a very pure surface. A similarly rapid initial stage was also observed by Adamsky[7] for silicon carbide in oxygen at 1500 °C. When most other authors have not observed a similar effect with silicon carbide, the probable reason is that they have used powder charges with the reactant gas passing across only the surface of the charge as discussed above.[3] The oxidation of silicon, on the other hand, usually is studied on planar samples. Deal and Grove[8] report a rapid initial oxidation of Si in dry oxygen, and they discuss the effect in terms of space charge within the silica layer. Alternatively one might speculate that the oxide at first forms as separate "islands" which after some time coalesce to a protective layer. In wet oxygen Deal and Grove[8] did not observe a rapid initial period; the reason for this difference between observations on Si and those given above for SiC is unknown.

Reaction rate in oxygen. The degree of reaction does not exceed 5 percent of the total SiC in any of the present runs, and it is therefore justified to treat the process as if it occurred on a plane surface. An oxide layer of thickness s growing by diffusion-controlled oxidation will have a growth rate, eqn. (6),

$$\frac{ds}{dt} = \frac{k}{s} \qquad (6)$$

which leads to the "parabolic law" $s^2 = 2kt + \text{const}$. The rate constant may conveniently be calculated from the differential form, eqn. (6). The surface area of the 20 mesh silicon carbide grains was estimated to 18.7 cm^2/g, or about 250 cm^2 for the 13.5 g samples. With an assumed density of 2.20 g cm^{-3} for the silica, the curve for run 6 in the interval from 5 to 20 h yields $k = 7.5 \times 10^{-10}$ cm^2 h^{-1} for oxidation in oxygen, which is in reasonable agreement with the value 5.0×10^{-10} cm^2 h^{-1} obtained at 1500 °C from the earlier plot of log k *vers.* $1/T$,[5] and which is thus considered a "normal" value. Runs 12 and 13 give values that are four to five times higher; this may be

connected with the fact that these runs were performed with reaction tubes that had previously been used for water vapour oxidation.

To be exact, the above value for the rate constant should be corrected for the pressure difference from 0.5 to 1 atm. The pressure dependence of the rate, however, is still a matter of debate (cf. below).

Reaction rate in water vapour. Subsequent to the initial rapid period, the rate in water vapour remains approximately constant, i.e. $ds/dt = k_w$. Runs 3 and 10 give $k_w = 5.7 \times 10^{-5}$ cm h^{-1} (for silica thicknesses of $0.5 - 1.0 \times 10^{-3}$ cm). After intermediate oxidation in oxygen the rate in water vapour appears somewhat lowered, with 3.4×10^{-5} cm h^{-1} found for the terminal period of run 7. Comparison with literature values appears difficult since most authors treat the oxidation of SiC in water vapour as diffusion-controlled and give parabolic rate constants, while such a treatment is not justified for the present observations.

Reaction in argon. The detrimental effect of heating silica bonded silicon carbide refractories in vacuum or inert gas has been known for some time, thus, Lukacs and Abrecht[9] emphasized that argon had the worst effect of the various atmospheres tried by them. The decreasing rate in the terminal part of run 13 is thought to be caused by increasingly poor contact between carbide and oxide as reaction (5) proceeds.

Rate laws and activation energies. Most investigators of the oxidation of silicon carbide have treated their data in terms of diffusion-controlled reaction. The results for the rate constants, however, show considerable scatter, and this is even more so for the temperature dependence of the rates. E.g. for the oxidation in dry oxygen, Schlichting[1] reports about 20 values for the activation energy, scattered over the range from 80 to 900 kJ/mol.

The situation appears better for the oxidation of silicon. Deal and Grove[8] presented a unified treatment taking into account both reaction control at the silicon − silica interface (linear rate) and diffusion control through the silica (parabolic), and they showed that experimental data for oxidation of silicon in both dry and wet oxygen over a wide range of temperatures correlated well with this treatment. The activation energies found by them were for the diffusion controlled oxidation by water 68 kJ/mol, for the diffusion controlled oxidation by oxygen 119 kJ/mol, and for the interface reaction 191 kJ/mol, the latter value being closely the same for water and oxygen oxidation of silicon.

A similar treatment has not been attempted for the oxidation of silicon carbide. It might also be more difficult in this case because of the larger spread in the data.

Diffusing species and pressure dependence. It is generally agreed that oxidation of silicon in oxygen, after a sufficient thickness of silica has been established, is rate limited by the diffusion of oxygen inwards through the silica. In the case of silicon carbide, some authors[10,11] have suggested that the rate is controlled by the outward diffusion of carbon monoxide. From the present observations it appears that this proposition may be rejected. Carbon monoxide is produced equally by the oxidation in water vapour, and yet this proceeds with a rate almost a factor of ten higher than that in oxygen. Thus we will maintain that both oxidation processes in dry oxygen are rate-controlled by diffusion of oxygen.

The nature of the diffusing oxygen species, however, has not been established. To quote from a recent paper by Tiller:[12] "For the past $10 - 15$ years a great debate has occurred over whether or not the Si oxidation process is controlled by the diffusion of charged or neutral species". Contribution to that debate is not a prime purpose of the present paper, and only some main points will be mentioned.

Jorgensen[13,14] showed that the oxidation of silicon in oxygen may be enhanced or stopped by the application of an electric field or its reverse across the silica layer. This seems conclusive evidence that the diffusing species are charged, most likely O^{2-} ions. Other authors[1] maintain that the rate is controlled by diffusion of molecular O_2. In support of the latter view it has been pointed out that the oxidation rate is proportional to the first power of the oxygen pressure, and some authors[1,15] have referred to one of the present authors[5] as the source of this information. It was written in that paper, however, that the available experimental evidence, including also the permeability measurements of Norton,[16] did not permit a clear-cut distinction between square-root and first-power pressure dependence. This appears to be true even to-day. There are other arguments, however, in favour of molecular diffusion.

At the time of the previous paper,[5] the author was inclined to believe in dissolution and transport of oxygen in the form of O^{2-} ions, with simultaneous transport of electrons from Si (or SiC) through the silica, in accordance with the well-established theory of Wagner[17] for the oxidation of metals. This view,

however, led to a puzzling problem in the case of silicon carbide oxidation: If the diffusing species in the oxide generally are ionic, how does one account for the outwards transport of CO ? Dissociation to oxygen and carbon ions seems unlikely. The problem is relieved if it is assumed that the gases dissolve and diffuse as molecules. Transport of O_2 molecules through silica glass in relation to the atomic dimensions in the glass structure has been discussed by Haul and Dümbgen.[18] The CO molecule is slightly smaller than O_2 and thus would be expected to diffuse more easily.

By oxidation of SiC by O_2, CO_2 is the equilibrium product in accordance with eqn. (1). This larger molecule might be expected to be nearly immobile in the silica lattice. When this apparently is not the case, the likely explanation is that the primary product at the SiC/SiO_2 interface is CO, and that the probability for its encounter with and oxidation by an O_2 molecule inside the silica is small because of the low concentration of both species.

The diffusion of neutral molecules appear contradictory to the observations by Jorgensen [14,15] on the effects of electric fields. The thorough discussions of Tiller [12] and of Mott [15] are aimed at a resolution of this conflict, but it appears that the matter is not yet settled.

The higher oxidation rate in water vapour is explained by the fact that the solubility of water in silica [19] is almost a factor of 1000 higher than that of oxygen [16] as already pointed out by Deal and Grove.[8] The dissolution most likely occurs by reaction to hydroxyl and the breaking of an oxygen bridge, formally written as eqn. (7). The solubility

$$-\overset{|}{Si}-O-\overset{|}{Si}-+H_2O = 2 -\overset{|}{Si}-OH \qquad (7)$$
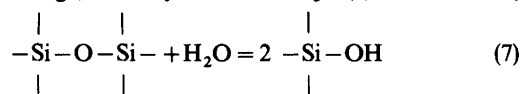
would then be expected to be proportional to the square root of water vapour pressure, as was demonstrated experimentally by Moulson and Roberts [19] for silica glass at 1000 °C. In the treatment of Deal and Grove, however, it was assumed that the solubility of water follows Henry's law, i.e., first-power dependence of pressure, and this was found consistent with experimental data for oxidation of Si in water vapour. Wolters [20] explained this apparent contradiction by the assumption of coupled transport of two hydrogen-bearing species. The data of Deal et al.[21] for relatively low partial pressures of water in oxygen, on the other hand, are consistent with a square-root dependence on the water vapour pressure as pointed out by Wolters.[20] In the present

experiments it appears that the rate of diffusion (or, more correctly, permeation) of water through the silica has been sufficiently rapid so that the oxidation rate essentially is controlled by the interface reaction, diffusion having only a small influence on the rates at the silica thicknesses in question.

It is interesting to note that the linear rate constant derived above for oxidation of SiC in water vapour at 1500 °C ($\sim 5 \times 10^{-5}$ cm h^{-1}) is much smaller than the linear rate constant found by Deal and Grove [8] for the water vapour oxidation of Si at 1200 °C (1.44×10^{-3} cm h^{-1}). This indicates that while the transport processes through the silica layer are similar for the oxidation of Si and of SiC, the interface reactions are different.

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