

#### IV. Discussion

It has been shown that aluminum nitride additions to alumina brought about the formation of a stable high-temperature  $\delta$ -alumina phase. The fact that this phenomenon escaped notice previously can be attributed to the fact that the usual thermal treatment of alumina is in an oxidizing atmosphere where aluminum nitride, if present, is readily oxidized. Nitrogen per se will not affect the alumina phase because the reaction between aluminum oxide and nitrogen is not favored thermodynamically.

Foster *et al.*<sup>6</sup> reported  $\delta$ -alumina as the alumina phase in aluminum oxide-aluminum carbide melts. These melts were studied in the temperature range 1800° to 2000°C. and the presence of a  $\delta$ -alumina phase was unexpected. They were unable, however, to establish responsibility for this  $\delta$ -alumina phase. Schneider and Gattow<sup>7</sup> observed a similar phase on burning aluminum in the presence of a carbonaceous promoter and attributed the stabilizing effect to carbon. None of these experiments was explicit enough to establish responsibility for the formation of  $\delta$ -alumina at high temperatures.

The addition of aluminum nitride to fused alumina yielded the  $\delta$ -alumina phase in the absence of a carbonaceous promoter. About 3% AlN was adequate to convert all the alumina to the  $\delta$  phase at 2050°C. Repeated fusion of this phase

continued to yield  $\delta$ -alumina as long as the nitrogen content was not reduced to a very low value. The  $\delta$  phase will transform to the  $\alpha$  phase on removal of the nitrogen.

The formation of  $\zeta$ -alumina with the addition of larger amounts of aluminum nitride to fused alumina completes the high-temperature crystal phases between Al<sub>2</sub>O<sub>3</sub> and AlN. There appears to be no other intermediate phase inasmuch as a mixture of  $\zeta$  and AlN was observed when the nitrogen content exceeded the 3.9% required for  $\zeta$ . The  $\zeta$  phase, like the  $\delta$  phase, will revert to the  $\alpha$  phase on removal of the nitrogen by oxidation.

The mechanism of these phase transformations in alumina containing aluminum nitride is not understood. Recognizing these effects may aid in the understanding of the complex aluminum oxide system.

<sup>6</sup> L. M. Foster, G. Long, and M. S. Hunter, "Reactions Between Aluminum Oxide and Carbon—The Al<sub>2</sub>O<sub>3</sub>-Al<sub>4</sub>C<sub>3</sub> Phase Diagram," *J. Am. Ceram. Soc.*, 39 [1] 1-11 (1956).

<sup>7</sup> A. Schneider and G. Gattow, "Zur Bildungswärme des Aluminiumoxyde" (Heat of Formation of Aluminum Oxide), *Z. anorg. u. allgem. Chem.*, 277 [1-2] 41-48 (1954); *Ceram. Abstr.*, 1958, September, p. 250c.

## Effects of Water Vapor on Oxidation of Silicon Carbide

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The rate of oxidation of silicon carbide was studied at different partial pressures of water vapor. The diffusion-rate constant was found to vary with the logarithm of the partial pressure of water vapor according to the theory of thin-film oxidation as proposed by Engell and Hauffe. The products of oxidation were cristobalite and tridymite, depending on the temperature. The diffusing species appeared to be the same in the presence of partial pressures of water vapor and in the presence of partial pressures of oxygen.

### I. Introduction

THE kinetics of the oxidation of silicon carbide have been studied quite extensively in the presence of air and oxygen,<sup>1</sup> and these studies have pointed out that the rate of oxidation follows a parabolic rate law. Jorgensen, Wadsworth, and Cutler<sup>2</sup> found that the parabolic rate constant

varied with the logarithm of the partial pressure of oxygen for thin-film oxidation and also found that a small amount of water vapor present in the oxidizing atmosphere greatly accelerated the rate of oxidation. Lea<sup>3</sup> made a brief survey

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<sup>1</sup> (a) A. C. Lea, "Silicon Carbide and Its Use as a Refractory Material," *Trans. Brit. Ceram. Soc.*, 40 [4] 93-118 (1941); *Ceram. Abstr.*, 21 [1] 16 (1942).

(b) T. H. Elmer and W. J. Koshuba, "Investigation of Oxidation of Silicon Carbide," NEPA Division Report No. 1768, Oak Ridge, Tennessee, March 1951 (unclassified).

(c) W. A. Lambertson, "Oxidation of Silicon Carbide," Carborundum Company report (unpublished).

(d) Guy Ervin, Jr., "Oxidation Behavior of Silicon Carbide," *J. Am. Ceram. Soc.*, 41 [9] 347-52 (1958).

(e) Hirohige Suzuki, "Study of Oxidation of Silicon Carbide Powder," *Yogyo Kyokai Shi*, 65 [736] 88-93 (1957); *Ceram. Abstr.*, 1958, January, p. 17a.

<sup>2</sup> P. J. Jorgensen, M. E. Wadsworth, and I. B. Cutler, "Effects of Oxygen Partial Pressure on Oxidation of Silicon Carbide," *J.*

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into the effects of different gases on the rate of oxidation of silicon carbide and noted that steam accelerated the rate of oxidation, but no satisfactory explanation was given. Three possible explanations were advanced, i.e.

- “(a) The volatilisation of silica in an air-steam atmosphere, or,
- (b) the hydrolysis of the coating, or,
- (c) modification by the atmosphere of the physical condition of the silica formed by the oxidation.”

Lea favored the explanation of hydrolysis of the oxide film.

Suzuki<sup>4</sup> also studied the role of steam in the oxidation of silicon carbide; he found that, in general, water vapor was an oxidizing agent for silicon carbide. The rate of oxidation was accelerated when water vapor was added to oxygen, and Suzuki proposed that possibly water vapor was accelerating the diffusion of oxygen, carbon monoxide, or carbon dioxide through the layer of SiO<sub>2</sub> or that water vapor promoting the transition of amorphous silica to cristobalite might account for the accelerated rate.

Water vapor undoubtedly has a marked effect on the rate of oxidation of silicon carbide. The effects of the partial pressure of water vapor on the oxidation of silicon carbide therefore were studied.

**II. Experimental Procedure**

A thermogravimetric apparatus was used to measure the rate of oxidation of silicon carbide; it consisted of a helical quartz spring, a Gaertner cathetometer, and an electric furnace heated by Kanthal-Super elements.

The equipment has been described<sup>5</sup>; for the present investigation the apparatus was modified, however, so that a controlled mixture of water vapor and argon could be passed through the furnace. The amount of water vapor present in the gaseous atmosphere was controlled by means of bubbling argon through water held at a constant temperature.

The use of water vapor as an oxidizing agent necessitated the heating of the quartz spring assembly to prevent condensation on the spring. The temperature of the spring assembly was held constant to ±1°C. by means of a separate controller.

The exit gases were bubbled through water in order to exert a slight positive pressure on the system. Fiberfrax was placed in the beginning of the hot zone of the furnace to heat the gases to the sample temperature.

The procedure for preparing the silicon carbide as a -325 +400-mesh powder was the same as that used in the previous work.<sup>5</sup>

**III. Discussion**

The rate of oxidation was measured at five different temperatures at various partial pressures of water vapor. Figure 1 shows the data obtained; each point on this figure represents the slope of a plot of the following equation which was found to be applicable to the oxidation of silicon carbide<sup>5</sup>:

$$[1 - (1 - R)^{1/2}]^2 = \frac{2\lambda^2}{r_0^2} k't \tag{1}$$

- R = fraction of reaction completed.
- λ = jump distance of diffusing species.
- k' = specific rate constant.
- t = time.
- r<sub>0</sub> = initial radius of silicon carbide particles.

Equation (1) is a modified form of the parabolic rate equation (x<sup>2</sup> = kt), where x is the thickness of the oxide film.

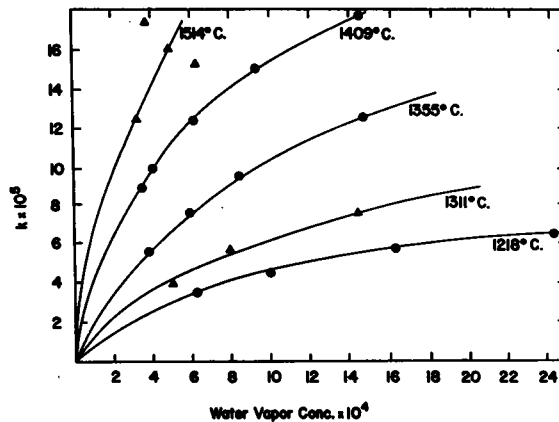


Fig. 1. Rate of oxidation at five different temperatures at various partial pressures of water vapor. Each point represents an experimental determination of the diffusion constant of equation (1) measured in reciprocal seconds.

The maximum value of R calculated from the thermogravimetric data was approximately 3%.

The curves of Fig. 1 are very similar to the curves obtained for the effects of the partial pressure of oxygen. A careful examination of the data pointed out that the rate of oxidation varied linearly with the logarithm of the partial pressure of water vapor. This indicated that water vapor acts similarly to oxygen in the oxidation of silicon carbide, and these results may be explained by the theory of thin-film oxidation proposed by Engell and Hauffe<sup>6</sup> or by the theory that the free energy for adsorption changes with the amount of surface covered.<sup>7</sup>

The theory of Engell and Hauffe describing the formation of thin oxide films involves the transport of cations through a film of thickness x to the surface and follows the parabolic law

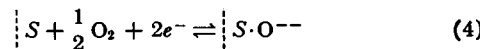
$$dx/dt = k/x \tag{2}$$

in which the constant k is defined as

$$k = \frac{V_m}{4N} n_x \nu_x \lambda^2 k' (\ln p_{O_2} + \ln n^4 K'^2) \tag{3}$$

- V<sub>m</sub> = molar volume.
- N = Avogadro's number.
- n<sub>x</sub> = number of diffusing cations.
- ν<sub>x</sub> = charge on cations.
- λ = jump distance.
- k' = specific rate constant.
- p<sub>O<sub>2</sub></sub> = partial pressure of oxygen.
- n = number of quasi-free electrons in system.
- K' = constant.

This equation was developed on the basis of equilibrium according to the following equation:



- { S = a surface site.
- { S · O<sup>--</sup> = a surface site with an adsorbed oxygen ion.

<sup>6</sup> (a) H. J. Engell and K. Hauffe, "Influence of Adsorption Phenomena on Oxidation of Metals at High Temperatures," *Metall*, 6 [11/12] 285-91 (1952).

(b) Progress in Metal Physics, Bruce Chalmers (editor), Vol. IV, p. 97. Interscience Publishers, Inc., New York, 1953.

<sup>7</sup> (a) M. A. Cook and A. G. Oblad, "Dynamic Mechanism of Heterogeneous Catalysis," *Ind. Eng. Chem.*, 45 [7] 1456-61 (1953).

<sup>4</sup> Hiroshige Suzuki, "Study on Oxidation of Silicon Carbide Powders: II, Effects of Steam on Oxidation of Silicon Carbide of Various Colors and Crystal Structures," *Yogyo Kyokai Shi*, 77 [7] 157-61 (1959).

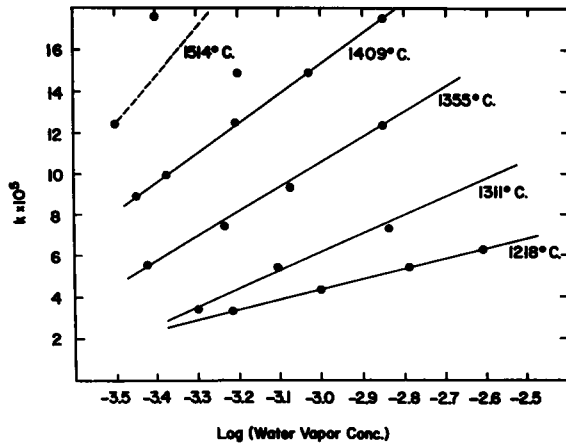
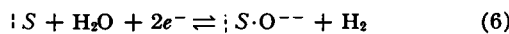


Fig. 2. Data from Fig. 1 showing logarithmic dependence on the partial pressure of water vapor, where  $k$  represents the experimentally determined rate constant in reciprocal seconds.

Let  $S_0$  be the total number of surface sites,  $N_{O^{--}}$  the number of surface sites with an oxygen ion adsorbed on the site, and  $n$  the number of electrons; writing the equation for the equilibrium constant, one then obtains

$$K_1 = \frac{N_{O^{--}}}{S_0 - N_{O^{--}}} \frac{1}{n^2(p_{O_2})^{1/2}} \quad (5)$$

In the case of water vapor, similar equations may be written, so that



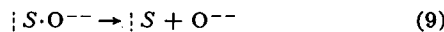
The equation for the equilibrium becomes

$$K_2 = \frac{N_{O^{--}} p_{H_2}}{(S_0 - N_{O^{--}}) n^2 p_{H_2O}} \quad (7)$$

Thus in developing the Engell and Hauffe theory for the oxidation of thin films in the case of water vapor, one must assume that the logarithm of the pressure of the hydrogen gas produced is negligibly small with respect to the logarithm of the pressure of the water vapor. Small amounts of  $H_2$  and  $CO_2$  were found in a sample of exit gases by using a mass spectrograph. If, however, a steady state is assumed, one may write



and



If  $k_1$  is the rate constant for equation (8), and  $k_2$  is the rate constant for equation (9), neglecting the reaction of hydrogen with the oxygen ion adsorbed on the surface site, one then has

$$\frac{dN_{O^{--}}}{dt} = k_1 S_0 p_{H_2O} n^2 - k_2 N_{O^{--}} \quad (10)$$

Equation (10) may be set equal to zero because of the assumption of the steady state, hence

$$\frac{k_1}{k_2} = K_2 = \frac{N_{O^{--}}}{S_0 n^2 p_{H_2O}} \quad (11)$$

Thus by using equation (7) assuming  $S_0 \gg N_{O^{--}}$  or by using equation (11), the Engell and Hauffe expression for the parabolic rate constant in the presence of water vapor

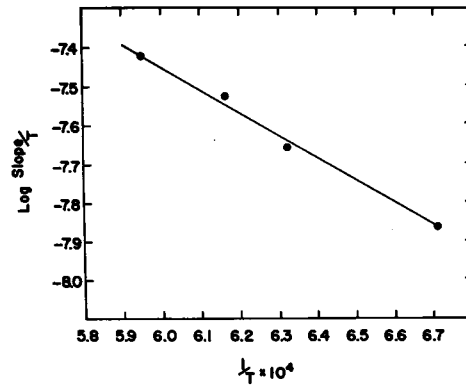


Fig. 3. Eyring plot used to calculate an energy of activation according to equation (12).

This equation may be written as

$$k = A \ln p_{H_2O} + B \quad (13)$$

$A$  and  $B$  = constants.

Thus a straight line should be obtained when plotting  $k$  versus  $\ln p_{H_2O}$ . This plot is shown in Fig. 2. The slopes of the lines shown in Fig. 2 contain the specific rate constant  $k'$ , and thus an activation energy may be obtained by plotting  $\ln(\text{slope}/T)$  versus  $1/T$ . The plot is shown in Fig. 3. The value of the activation energy for diffusion was 24.4 kcal. per mole.

The data for the 1514°C. isotherm in Fig. 2 were extremely difficult to obtain; therefore a dashed line is drawn for this isotherm. The slope of this line was obtained by extrapolating the data of Fig. 3.

Almost the same results as those from the Engell and Hauffe theory may be derived on the basis that the free energy for the adsorption process depends on the surface coverage as follows:

$$\Delta F = \Delta F_0 + \alpha \theta \quad (14)$$

where  $\alpha$  is a proportionality constant with the units necessary to convert  $\theta$ , the fraction of the surface covered, to units of free energy.

This theory was derived in detail previously<sup>2</sup> for oxygen; for water vapor, the parabolic rate constant becomes

$$k = \frac{k_0 \lambda^2 k' A R T}{\alpha} (\ln p_{H_2O} + \ln K_0) \quad (15)$$

$k_0$  and  $K_0$  = constants.

$\lambda$  = jump distance of diffusing ions.

$A$  = surface area.

$R$  = gas constant.

The slope of equation (15) contains  $T^2$ ; hence a plot of  $\ln(\text{slope}/T^2)$  versus  $1/T$  allows the activation energy to be calculated. The plot is shown in Fig. 4, and the value of the activation energy according to this model was 21.1 kcal. per mole. Equation (15) can be used to obtain the value of the energy of adsorption of the water vapor on the surface sites. The intercept of a plot of equation (15) divided by the slope gives the following relation:

$$\text{Intercept/slope} = \ln K_0$$

$$\ln K_0 = \frac{-\Delta H_0}{RT} + \frac{\Delta S_0}{R} \quad (16)$$

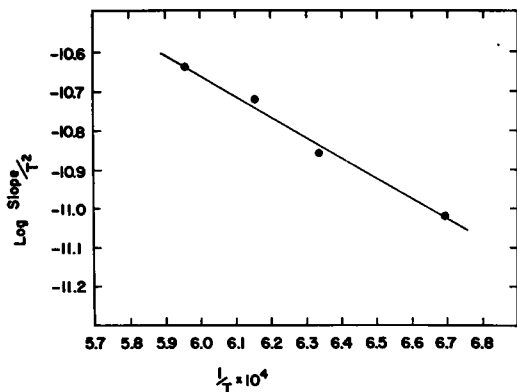


Fig. 4. Eyring plot used to calculate an energy of activation according to equation (15).

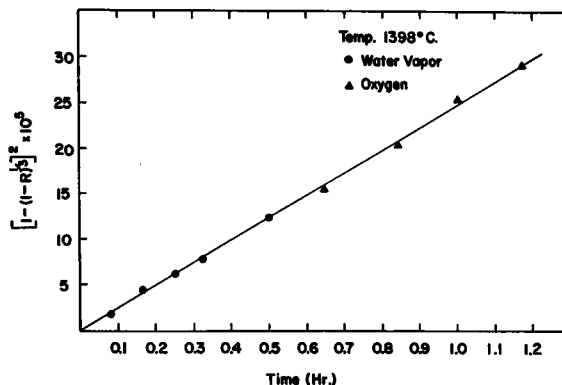


Fig. 6. Comparison of the rates of oxidation of silicon carbide in the presence of water vapor and in the presence of oxygen at 1398°C.

value of 19.2 kcal. per mole was obtained for the energy of adsorption on the silica film. The positive enthalpy of adsorption is very unlikely and casts much doubt on this model as an explanation for the oxidation of silicon carbide.

In Fig. 5, the point corresponding to the temperature of 1218°C. does not fall on the line, which indicates a change in the system. Samples from each of the isotherms were analyzed using an X-ray diffractometer; the samples oxidized at 1218°C. were found to be the cristobalite form of silicon dioxide, whereas samples from the other isotherms oxidized to tridymite.

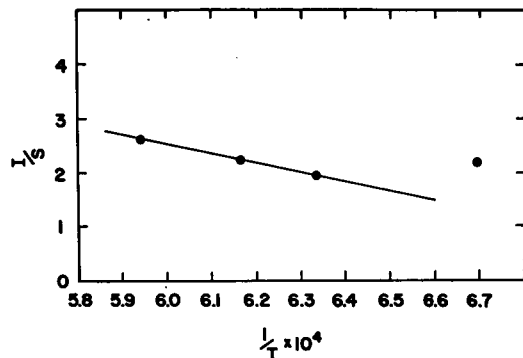
The main problem involved in studying a diffusion problem is to identify the diffusing species. The diffusing species in the case of the oxidation of silicon carbide may be  $O_2$ ,  $CO$ , or  $CO_2$  as suggested by Suzuki<sup>4</sup> or may be oxygen ions diffusing in, carbon ions diffusing out, or silicon ions diffusing out. Diffusion of  $O_2$ ,  $CO$ , and  $CO_2$  was ruled out on the basis that the activation energy obtained in this study was too great for molecular diffusion. The diffusion of oxygen atoms was eliminated because the kinetic data did not correspond to the correct partial pressure of oxygen dependence. Carbon ions do not seem to be the diffusing species when the value of the energy of activation for the oxidation of silicon, 45 kcal. per mole,<sup>8</sup> is compared with that of silicon carbide, 48.8 kcal. per mole. The diffusing species

therefore may be oxygen ions or silicon ions and more data are necessary to distinguish between them.

The difference in the activation energy between silicon carbide oxidized in partial pressures of water vapor and silicon carbide oxidized in partial pressures of oxygen may be attributed either to a change in the film from an amorphous phase to a crystalline phase or to a change in the diffusing species. An experiment therefore was conducted to compare the rate of oxidation of SiC in water vapor with the rate of its oxidation in oxygen when a crystalline film was present. This was accomplished by first oxidizing the silicon carbide in water vapor to produce a tridymite film and then changing to oxygen at the same partial pressure as the water vapor. A plot of the data obtained is shown in Fig. 6. The circles indicate the data obtained in water vapor and the triangles indicate the data obtained in oxygen. Note that the rate, which is the slope of the line, is constant. It is most likely, therefore, that the diffusing species is the same in the presence of water vapor and in the presence of oxygen, and the difference in the rate of oxidation in water vapor and in partial pressures of oxygen is due to the change in the nature of the oxide film. This may possibly be accounted for by a change from bulk diffusion to grain-boundary diffusion.

#### IV. Conclusions

The following conclusions may be drawn from the data presented in this paper: (1) The rate of oxidation of silicon carbide depends on the water-vapor pressure. (2) The silicon dioxide film in a water-vapor atmosphere is either tridymite or cristobalite. (3) The mechanism of thin-film oxidation proposed by Engell and Hauffe correlates the kinetic data for the oxidation of silicon carbide in the presence of water vapor. (4) The model of change in free energy with the amount of surface covered does not fit the oxidation of SiC in water vapor and tends to discount this model for the oxidation of SiC in the presence of partial pressures of oxygen. (5) The diffusing species is the same in the presence of partial pressures of water vapor and in the presence of partial pressures of oxygen.



<sup>8</sup> (a) J. T. Law, "High-Temperature Oxidation of Silicon,"