

# **Passive-Oxidation Kinetics of SiC Microparticles**

D. Das,<sup>†</sup> J. Farjas,<sup> $\ddagger$ ,¶</sup> and P. Roura<sup> $\ddagger$ </sup>

Department of Physics, Ramakrishna Mission Residential College, Narendrapur, Kolkata-700103, India GRMT, Department of Physics, University of Girona, Campus Montilivi, E17071 Girona, Catalonia, Spain

We investigated the oxidation kinetics of SiC materials in the form of powders (average dimension 4  $\mu$ m) in the temperature range 1100°–1500°C in dry air. The oxidation process was monitored through the relative mass gain in a thermobalance. As the specific surface area of the particles was measured, the recorded mass gain could be converted into the corresponding oxide thickness. The oxidation isotherms were fitted to a linear-parabolic equation, and the parabolic rate constant was evaluated. Up to 1400°C, temperature dependence can be described by a single activation energy of 179 kJ/mol, which increases in the 1400°–1500°C temperature range. These results are compared with the oxidation behavior of sintered polycrystalline and monocrystalline SiC materials.

## I. Introduction

ONTROP SIDATION behavior of SiC materials (in the form of powders,<sup>1</sup> polycrystalline sintered ceramics,<sup>2,3</sup> CVD films,<sup>3–5</sup> and platelets<sup>6</sup>) has been the subject of considerable interest for more than half a century. Their kinetics are usually described by the diffusion-reaction model, which was developed by Deal and Grove<sup>7</sup> for the simpler case of monocrystalline silicon. According to this model, a linear-parabolic equation relates the oxide thickness, *X*, to the oxidation time, *t*:

$$X^{2} + AX = B(t + t_{0})$$
(1)

where B/A and B are the linear and parabolic rate constants, respectively, and  $t_0$  accounts for any initial oxide layer or for deviations from the linear-parabolic kinetics at short times.

Studies on monocrystalline SiC have produced accurate values for these constants,<sup>5</sup> which are related to the reaction rate at the SiC–SiO<sub>2</sub> interface and the diffusion coefficient of oxygen through the SiO<sub>2</sub> layer. The linear constant is important only at low temperatures and has been quantified up to  $1100^{\circ}$ C.<sup>5</sup> The absolute value of the parabolic constant agrees with that found in silicon<sup>3</sup> for temperatures <1400°C, and it is consistent with the diffusion of molecular oxygen in vitreous silica. At >1400°C, the activation energy increases, indicating a change in the transport mechanism.<sup>8</sup> At these high temperatures, atomic oxygen would be the diffusing species.<sup>9</sup> Compared with crystalline silicon, oxidation of SiC is much more dependent on crystal orientation, the C-terminated surface being oxidized faster than the silicon-terminated one.<sup>3,5,6,10</sup>

There is considerable scattering in the oxidation rates of sintered SiC materials,<sup>2</sup>owing primarily to the effect of impurities

Manuscript No. 10163. Received April 29, 2003; approved February 17, 2004. Supported by the Spanish Programa Nacional de Materiales under contract No. MAT2002-04263-C04-02.

<sup>†</sup>Ramakrishna Mission Residential College. <sup>‡</sup>GRMT on the transport properties of the oxide and to the preferential crystal orientation of individual grains. Despite these complications, the observed temperature dependence of polycrystalline materials can be understood as the result of an average of the temperature dependencies of individual crystal orientations.<sup>3</sup>

The oxidation of powdered SiC is much more poorly understood from the quantitative point of view. Two conflicting values of the activation energy (85 and 180 kJ/mol) were reported by Jorgensen *et al.* in two papers<sup>1,11</sup> that describe experiments conducted on the same powders. In fact, those experiments were not analyzed within the framework of the Deal and Grove model and, consequently, they should be reanalyzed to be able to compare them to the more recent experiments on monocrystals. Unfortunately, the surface area of the powders was not measured. This means that, at most, only the activation energy could be extracted from their work, but no information can be obtained concerning the absolute value of the oxidation rate. To our knowledge, this limitation is common to all the papers on SiC powders published before those of Jorgensen (see the list of references therein).<sup>1</sup> We have found only two more papers on SiC powders published since then: Pultz<sup>12</sup> reported an enormous activation energy for the parabolic constant rate of 630 kJ/mol on SiC microparticles with high contents of free silicon and carbon and, more recently, Yoshimura et al.13 studied oxidation of SiC by high-pressure H<sub>2</sub>O.

A summary of the activation energies for a number of SiC materials has been published recently.<sup>14</sup> The work we present here is intended to bridge the gap between the earlier SiC oxidation experiments, conducted on powders, and the more recent and more accurate experiments on monocrystals and sintered materials.

#### **II. Experimental Procedures**

We used crystalline SiC in the form of pale-green micropowders. By means of optical microscopy, the dimension of the particles was found to vary between 2 and 7 µm, with the average dimension being  $\sim 4 \mu m$ . Using scanning electron microscopy (SEM), it was observed that the particles had smooth surfaces, sharp edges, and irregular shapes (Fig. 1). The specific surface area of the particles, measured by the gas adsorption technique, was found to be  $S = 1.273 \text{ m}^2/\text{g}$ , which, if spherical, would correspond to a mean diameter of 1.5 µm. Although it is smaller than the value obtained by microscopy, this is not surprising because a particle with an irregular shape has a surface area that corresponds to a smaller spherical particle. Using X-ray diffraction (XRD) (Fig. 2), the crystalline phases of the particles were shown to be hexagonal and rhombohedral, with a possible minor presence of the cubic phase. The relative intensity of the peaks, centered at  $2\theta = 65.67$ (for the rhombohedral [1 0 9] planes) and 64.5 and 66.9 (for the hexagonal [1 0 22] and [0 1 23] planes), indicates that the rhombohedral phase is the dominant phase.

The initial chemical composition near the outer surface of the particles was analyzed by X-ray photoelectron spectroscopy (XPS) before and after sputtering (for a short duration) with a 5 kV beam of argon ions. The results are detailed in Table I. The peak energies correspond quite well to the values found in the literature. For instance, one can compare the O-Si binding energy of 533.0 eV

H. Du-contributing editor

 $<sup>^{\</sup>P}\!Author to whom correspondence should be addressed. e-mail: jordi.farjas@udg.es.$ 



Fig. 1. SEM images of SiC microparticles: (a) before oxidation, (b) after oxidation at 1400°C for 1 h, (c) after oxidation at 1500°C for 1 h. Size of images: 9.4  $\mu$ m × 9.8  $\mu$ m.

with the peak position in Fig. 3. Although a quantitative value of the initial  $SiO_2$  layer thickness on the surface of the particles cannot be given with accuracy, the detection of an important signal due to Si-C bonds in the initial condition (before sputtering) indicates that it should be thinner than 10 nm. The atomic concentration (Table I) is consistent with a two-phase material consisting of stoichiometric SiC and SiO<sub>2</sub>. The absence of any silicon or carbon precipitate has been assessed by Raman spectroscopy. Finally, the presence of impurities in the bulk was analyzed semiquantitatively by X-ray fluorescence, which gave a low concentration of Ti (0.09%), V (0.01%), and Zr (0.008%).

The oxidation experiments were performed with thermobalance (TGA/SDTA 851, Mettler-Toledo, Hightstown, NJ). A high-purity mixture of nitrogen and oxygen (oxygen partial pressure, 0.17 atm) was used as the oxidation gas (water vapor content <5 ppm). To minimize the heating time of the powders, we introduced the sample powder (kept in a high-purity alumina crucible) into the furnace of the TG at the temperature of the oxidation experiments, so that we could record the early stages of oxidation through the related increase of mass. However, there could be some error in the recorded mass at the beginning. The nonsteady situation that would occur when the furnace is opened at



**Fig. 2.** XRD difractogram. The higher intensity of the secondary peak of rhombohedral SiC (solid arrow) indicates that it is more abundant than the hexagonal form (dashed arrows).

high temperature to introduce the crucible and then closed causes an oscillation of the balance arm, which may last 2–3 min. In addition, thermalization of the crucible and the powders at the furnace temperature may take some time. Thus, to assess the reliability of recorded mass variation curves, the total mass change recorded by TG was compared with the difference between the masses measured at room temperature before and after every oxidation experiment. With a typical initial mass of 50 mg, the mass gain could be recorded within an error bar of  $\pm$ 50 µg. All thermograms were corrected by the blank curve of the apparatus under the same experimental conditions.

Scanning electron microscopy (SEM) images of the powder particles were taken before and after oxidation (Fig. 1), to evaluate probable systematic error in the oxidation results from the rounding of particles with oxidation time or from the sintering of particles at high temperatures. We found that, under the oxidation conditions, the shape of particles was significantly changed only at  $1400^{\circ}$  and  $1500^{\circ}$ C.

# III. Results

We recorded the mass gain due to oxidation for 1 h at several temperatures (from  $1100^{\circ}-1500^{\circ}$ C). To carry out a direct comparison with results reported by other authors on the oxidation of single-crystal and polycrystalline SiC, we converted the mass gain into the corresponding oxide layer thickness ( $\Delta X$ ). This conversion can be done quite easily if the specific surface area (*S*) is known and assuming that the number of silicon atoms is conserved during oxidation. The following relationship is obtained:

$$\Delta X = \frac{1}{S} \rho_{\rm SiO_2} \frac{m_{\rm SiO_2}}{m_{\rm SiO_2} - m_{\rm SiC}} m_{\rm r} \tag{2}$$

where  $\rho_{SiO2}$  is the density of SiO<sub>2</sub> (2.20 g/cm<sup>3</sup>);  $m_i$  is the molecular mass ( $m_{SiC} = 40.1, m_{SiO2} = 60.1$ ), and  $m_r$  is the relative mass gain (i.e., the mass gain relative to the initial mass of the powder,  $m_r \equiv \Delta m/m_0$ ). For our particular powder,

$$\Delta X(\text{in nm}) = 1309 \, m_{\text{r}} \tag{3}$$

This proportionality would be exact if the surface area of the SiC particle core (below the oxide layer) remained constant.

Table I.Atomic Concentration (%)Determined by XPS

Sputtering time (min)	C (1s)	O (1s)	Si (2p)
0	46.98	18.93	34.09
1	46.20	9.80	44.00
2	47.00	3.86	49.14





Fig. 3. XPS spectrum of the O (1s) peak. Its position corresponds quite well to the O-Si bond (533.0 eV).

In Fig. 4, the oxidation thermograms obtained at all temperatures are shown. To look at deviations from purely parabolic kinetics,  $\Delta X$  has been plotted versus  $t^{1/2}$ , and the curves are compared with a straight line (dashed). At times <1-2 min, the results are not reliable because of initial thermal and mechanical instabilities, so we restrict our analysis to longer times. At  $>1300^{\circ}$ C, curves are convex with a slope that diminishes at longer times, this effect being more pronounced at  $1500^{\circ}$ C. One might



Fig. 4. Oxidation thermograms measured with a thermobalance. The experimental curves (solid) are compared with straight lines (dashed), which correspond to perfect parabolic kinetics. The best fits to a linear-parabolic kinetics are also plotted (dotted curves).

think that this reduction in the apparent oxidation rate is related to a diminution of the specific surface area, S. However, this is not the case. The formation of a SiO<sub>2</sub> layer of thickness  $\Delta X$  consumes a SiC layer of  $\Delta X/2$ . Therefore, at 1500°C, 80 nm of SiC are consumed after 1 h. This corresponds, roughly, to a diminution of S by 8%, whereas the oxidation rate is reduced by 30%. (This estimation is done by considering that particles are spherical. For the real shapes observed by SEM, the reduction of S would be smaller.) A simpler interpretation of this slower oxidation comes from the SEM micrographs obtained after oxidation at 1400° and 1500°C (Fig. 1). Sintering of the particles due to viscous flow of amorphous  $SiO_2$  is apparent at both temperatures. As a result, the average diffusion path of O<sub>2</sub> leading to the SiC core is longer and therefore oxidation is slower. At <1300°C, the curves are concave. After fitting, it will become clear that this feature is caused by the contribution of a linear term (AX in Eq. (1)).

To extract the kinetic parameters, these curves should be analyzed according to the linear-parabolic Eq. (1). However, this equation does not correspond exactly to our experiments because, in our case, the absolute value of the oxide thickness, X, is not known. By XPS analyses we know that, in their initial state, the particles are covered by a thin layer of oxide. Hence, the oxide thickness can be calculated by simply adding this unknown initial thickness,  $X_0$ , to  $\Delta X$ :

$$X = \Delta X + X_0 \tag{4}$$

By introducing Eq. (4) into Eq. (1) we obtain a linear-parabolic equation for  $\Delta X$ :

$$(\Delta X)^2 + A' \Delta X = B(t - t_0')$$
<sup>(5)</sup>

where the parabolic rate constant *B* coincides with that of Eq. (1), but:

$$A' = A + 2X_0 \text{ and } t_0' = t_0 - \frac{AX_0 + X_0^2}{B}$$
 (6)

This analysis indicates that the parabolic rate constant can be obtained with confidence, even in the case of an initial oxide layer, whereas the linear rate constant (B/A') is only reliable if  $X_0$  is small enough.

The best fits to the linear-parabolic kinetics (Eq. (5)) are plotted as dotted lines in Fig. 4. After roughly 1 s, the coincidence with the experimental curves is so good that, in fact, the calculated ones are hidden. One exception is the curve of  $1500^{\circ}$ C, for which it has not been possible to reach reasonable agreement at long times. The fitting parameters *B* and *A*<sup>'</sup> are detailed in Table II.

For 1500° and 1400°C, A' took unrealistic negative values because, at these high temperatures, sintering modifies the simple oxidation kinetics of Eq. (5). Additionally, in single-crystal SiC samples, oxidation experiments at >1200°C are fitted with a simple parabolic kinetics.<sup>8</sup> Consequently, the values of *B* reported in Table II for 1500° and 1400°C are obtained from the slope of the experimental curves at short times, where sintering is less significant. The temperature dependence of the parabolic rate constants is shown in Fig. 5. A single activation energy of 179 kJ/mol (1.86 eV) is obtained for the temperatures <1500°C.

Table II. Kinetic ParametersObtained after Fitting Mass GainCurve to a Linear-Parabolic Equation

<i>T</i> (°C)	$B \text{ (nm}^2/\text{min)}$	A' (nm)
1100 1200 1300 1400 1500	8.8 27.8 69.6 153 510	14.1 20.6 6.1



**Fig. 5.** Arrhenius plot of parabolic rate constants: our results (solid crosses), and parabolic rate constants from Costello and Tressler<sup>3</sup> (open symbols) for three types of polycrystalline materials (converted to oxygen partial pressure = 0.17 atm).

## IV. Discussion

In this section, we will try to explain the oxidation behavior observed in SiC powder in light of the behavior of monocrystalline and polycrystalline SiC materials reported in the literature. In contrast with most of the results published, which correspond to hexagonal SiC, several phases coexist in our powder. This fact does not add any further complications because, as shown by Ramberg *et al.*,<sup>5</sup> different crystalline phases oxidize at the same rate. Thus, in principle, the main difference between our powder and the monocrystalline material is the simultaneous oxidation of a number of crystal orientations and, in fact, we will see that the oxidation rate can be understood as an average value of these.

In contrast with the experiments of Jorgensen et al.<sup>1</sup> on SiC powders, we can compare the absolute values of oxide thickness and oxidation rate with those of polycrystalline materials because we measured the surface area. In Fig. 6, our oxidation curves are plotted in a log-log scale and compared with those measured by Costello et al.<sup>3</sup> on sintered  $\alpha$ -SiC in an oxygen partial pressure of 1 atm. Their values for oxide thickness have been converted to fit 1 atm. Their values for oxide unconess have been 11 our experimental conditions by considering that, near  $P_{O2} = 1$  atm, the parabolic rate constant is nearly proportional to  $P_{O2}^{-1/2,15}$  and, consequently, the thickness grows proportionally to  $P_{O2}^{-1}$ . We see that, at any temperature, the thicknesses are very similar, differing by <15%. This difference is very small considering that, in polycrystalline materials, the oxidation rate can be modified by a number of structural parameters, such as a particular preferential grain orientation or by the effect of impurities, which may increase the oxidation rate.<sup>16</sup> In the case of sintered  $\alpha$ -SiC (rhombs in Fig. 5), the higher impurity content usually found in sintered SiC does not result in any significant difference in oxide thickness (Fig. 6) nor in the parabolic rate constant, B (Fig. 5). On the other hand, the high-impurity content could explain the higher oxidation rates for the other SiC sintered materials (Fig. 5).

The results obtained by Costello *et al.*<sup>3</sup> show oxidation curves that lie somewhere between those corresponding to the oxidation of the slow and fast faces of single crystal SiC. In our powders, the result is similar (Fig. 6) and can be interpreted by simply considering that the measured oxide thickness is the average among individual crystal orientations. At 1200°C, our curve is located slightly higher than the arithmetic mean of the fast and



**Fig. 6.** Oxidation isotherms in logarithmic scales (solid lines). Comparison with those from Costello and Tressler<sup>3</sup> (dashed lines) for one sintered polycrystalline material (converted to the oxygen partial pressure of 0.17 atm). Circles and filled triangles correspond to the oxidation monocrystalline SiC at 1400° and 1200°C,<sup>3</sup> respectively, and empty triangles are the arithmetic mean at 1200°C.

slow faces. At 1400°C, our result approaches, at long times, the slow face curve due to the sintering of particles discussed in the previous section. Oxidation kinetics could be slower than expected at high temperature because of two additional processes, namely: (i) SiO<sub>2</sub> crystallisation and (ii) CO<sub>2</sub> bubbling at the SiC-SiO<sub>2</sub> interface. The reduction of oxidation rate by crystobalite formation would be relevant only for impure silica layers.<sup>8</sup> Additionally, the reported times needed for silica crystallization<sup>1,17</sup> are much longer than they were in our oxidation experiments. It will be shown below that, if present at all, the amount of crystobalite in our samples at the end of any experiment was low. Concerning formation of bubbles, it may be possible at >1300°C.18 These bubbles could eventually burst somewhere on the amorphous oxide layer, leaving small SiO<sub>2</sub> debris similar to those shown in the micrograph after oxidation at 1500°C (Fig. 1) (this fact is described in ref.<sup>19</sup> although no micrograph, which could be compared with ours, is shown). However, the lack of carbon precipitates in the SiC particles would diminish the possibility of bubble formation.18

The Arrhenius plot of the parabolic rate constant, *B*, (Fig. 6) can be fitted with a single activation energy of  $179 \pm 4$  kJ/mol up to 1400°C, which increases at 1500°C. This evolution is roughly followed by sintered materials. However, in this case, the higher dispersion of the individual values of *B* for any particular material and among different materials, obscured this increase of the activation energy in the original work of Costello *et al.*<sup>3</sup> Ramberg *et al.*<sup>8</sup> have shown that it corresponds to the transition from two different transport mechanisms of oxygen through the silica layer: O<sub>2</sub> permeation at low temperature and atomic oxygen network diffusion at high temperature. This transition is observed in amorphous silica but not in crystallized layers.<sup>8</sup> Therefore, if initiated, crystallization is far from completion in our samples at 1500°C.

The value of the activation energy should be compared with the values obtained from monocrystalline SiC. The oxidation kinetics of SiC monocrystals is very different, depending on crystal orientation. For the so-called fast-oxidation-face (silicon-terminated face), an activation energy of 99 kJ/mol is obtained,<sup>5</sup> whereas a value of 292 kJ/mol holds for the slow-oxidation-face (C-terminated).<sup>5</sup> Hence, the intermediate value of 179 kJ/mol in

powders can be explained as an average between the activation energies of both faces, because multiple faces are exposed to oxidation for any individual particle.

Finally, when compared with the previous experiments on SiC powders,<sup>1,11</sup> our activation energy is slightly lower than the 190 kJ/mol obtained in Ref. 11. The much smaller value of 85 kJ/mol<sup>1</sup> was obtained with a model of diffusion in solids that, in view of this discrepancy, does not apply to SiC and, consequently, this value has to be discarded.

### Acknowledgments

We are grateful to Lorenzo Calvo, Xavier Alcover, and Tariq Jawari of the Serveis Científico-Tècnics of the University of Barcelona for the chemical analyses, X-ray diffraction, and Raman spectroscopy, respectively.

#### References

<sup>1</sup>P. J. Jorgensen, M. E. Wadsworth, and I. B. Cutler, "Oxidation of Silicon Carbide," J. Am. Ceram. Soc., 42, 613–16 (1959).

<sup>2</sup>J. A. Costello and R. E. Tressler, "Oxidation-Kinetics of Hot-Pressed and Sintered Alpha-SiC," J. Am. Ceram. Soc., **64**, 327–31 (1981).

<sup>3</sup>J. A. Costello and R. E. Tressler, "Oxidation-Kinetics of Silicon-Carbide Crystals and Ceramics. Part I. In Dry Oxygen," *J. Am. Ceram. Soc.*, **69**, 674–81 (1986).

<sup>4</sup>T. Narushima, T. Goto, and T. Hirai, "High-Temperature Passive Oxidation of Chemically Vapor-Deposited Silicon-Carbide," *J. Am. Ceram. Soc.*, **72**, 1386–90 (1989). <sup>5</sup>C. E. Ramberg, G. Cruciani, K. E. Spear, and R. E. Tressler, "Passive-Oxidation

C. E. Ramorg, O. Chetani, K. E. Spear, and K. E. Hessler, Passive-Oxidation Kinetics of High-Purity Silicon Carbide from 800 Degrees to 1100 Degrees C," J. Am. Ceram. Soc., 79, 2897–911 (1996). <sup>6</sup>R. C. A. Harris, "Oxidation of 6H-Alpha Silicon-Carbide Platelets," J. Am. Ceram. Soc., 58, 7–9 (1975).

<sup>7</sup>B. E. Deal and A. S. Grove, "General Relationship for Thermal Oxidation of Silicon," J. Appl. Phys., 36, 3770–78 (1965).

<sup>8</sup>C. E. Ramberg and W. L. Worrell, "Oxygen Transport in Silica at High Temperatures: Implications of Oxidation Kinetics," *J. Am. Ceram. Soc.*, **84**, 2607–16 (2001).

<sup>9</sup>Z. Zheng, R. E. Tressler, and K. E. Spear, "Oxidation of Single-Crystal Silicon-Carbide Part I. Experimental Studies," *J. Electrochem. Soc.*, **137**, 854–58 (1990).

<sup>10</sup>B. Hornetz, "ARXPS Studies of SiO2-SiC Interfaces and Oxidation of 6H SiC Single-Crystal Si-(001) and C-(001)Over-Bar Surfaces," *J. Mater. Res.*, **9**, 3088–94 (1994).

<sup>(1594).</sup> <sup>11</sup>P. J. Jorgensen, M. E. Wadsworth, I. B. Cutler, "Effects of Oxygen Partial Pressure on the Oxidation of Silicon Carbide," *J. Am. Ceram. Soc.*, **43**, 209 (1960).

<sup>12</sup>W. W. Pultz, "Temperature and Oxygen Pressure Dependence of Silicon Carbide Oxidation," J. Phys. Chem., 71, 4556–8 (1967).

<sup>13</sup>M. Yoshimura, J. Kase, and S. Somiya, "Oxidation of SiC Powder by High-Temperature, High-Pressure H<sub>2</sub>O," *J. Mater. Res.*, **1**, 100–103 (1986).

<sup>14</sup>T. Shimoo, F. Toyoda, and K. Okamura, "Oxidation Kinetics of Low-Oxygen Silicon Carbide Fiber," J. Mater. Sci., 35, 3301–06 (2000).

<sup>15</sup>Z. Zheng, R. E. Tressler, and K. E. Spear, "Oxidation of Single Crystal Silicon Carbide: II, Kinetic Model," *J. Electrochem. Soc.*, **137**, 2812–16 (1990).

<sup>16</sup>E. Opila, "Influence of Alumina Reaction Tube Impurities on the Oxidation of Chemically-Vapor-Deposited Silicon-Carbide," *J. Am. Ceram. Soc.*, **78**, 1107–10 (1995).

<sup>17</sup>L. U. J. T. Ogbuji, "Effect of Devitrification on Oxidation Kinetics of SiC," *J. Am. Ceram. Soc.*, **80**, 1544–50 (1997).

<sup>18</sup>D. M. Mieskowski, T. E. Mitchell, and A. H. Heuer, "Bubble Formation in Oxide Scales of SiC," J. Am. Ceram. Soc., **67**, C17–C18 (1984).

<sup>19</sup>B. Schneider, A. Guette, R. Naslain, M. Cataldi, and A. Costecalde, "A Theoretical and Experimental Approach to the Active-to-Passive Transition in the Oxidation of Silicon Carbide," *J. Mater. Sci.*, **33**, 535–47 (1998).