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Oxidation kinetics of silicon carbide whiskers studied by X-ray photoelectron spectroscopy

PU SEN WANG, S. M. HSU
Ceramics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
T. N. WITTBERG
University of Dayton Research Institute, Dayton, Ohio 45469, USA

Silicon carbide whisker surfaces were characterized by X-ray photoelectron spectroscopy (XPS) to determine changes in the surface oxide film which occurred as a result of heating in air at temperatures from 600 to 800 °C. Equations were derived for the calculation of surface oxide film thickness from the SiC to SiO_2 2p intensity ratios. Oxidation was found to follow a linear rate law in this temperature range for the first 10 nm of oxide growth. An activation energy of 17.2 ± 2.8 kcal mol^{-1} (72 ± 12 kJ mol^{-1}) was measured.

1. Introduction

Silicon carbide whiskers and fibres are now widely used in ceramic-matrix composites, reinforced glass, and metal-matrix composites. In these composite materials, the interface strength and bonding between the SiC fibres and the matrix are critical in determining their reliability and durability. Powders of silicon carbide are the basis for high-strength ceramic components which are formed by sintering. The presence of an oxide layer on the surface of the SiC powder particles can be detrimental to the sintering process [1].

The oxidation kinetics for silicon carbide have been the subject of a number of studies [2–5]. Early work showed that the oxidation of silicon carbide powders in O_2 follows a parabolic rate law between 1200 and 1500 °C [2]. More recently, the oxidation of single-crystal silicon carbide has been studied [3–5]. In all three of these single-crystal studies, the oxidation rate was found to be higher on the carbon-rich $(000\bar{1})$ face than on the silicon-rich (0001) face. In one of these studies, the oxidation of polycrystalline SiC materials was also examined [5]. The oxidation rates and activation energies for these polycrystalline materials were found to be intermediate between those observed for fast- and slow-growth faces of the single-crystal material.

The surface-sensitive technique of X-ray photoelectron spectroscopy (XPS) has been used to analyse a number of commercially available SiC powders and whiskers [1, 6]. Varying amounts of SiO_2 and hydrocarbons (or free carbon) were found on the surfaces of these materials. In general, the SiC whiskers were found to have higher surface oxygen levels than the powders [6]. Other contaminants which were detected on these materials appeared to be related to the particular methods of processing.

In the present study, XPS has been used to study the oxidation of silicon carbide whiskers in air at temperatures between 600 and 800 °C. Previous studies on the oxidation of SiC have been restricted, in most cases, to temperatures above 900 °C because of the inability to measure the thickness of SiO_2 layers less than 10 nm thick. At lower temperatures, the surface chemical reaction will be the dominant rate-determining step and so a linear rate law should apply. A previous study has also shown only a slight difference in the oxidation rates for hot-pressed silicon carbide heated in dry as opposed to wet oxygen [7]. For this reason it seems appropriate to study the oxidation of silicon carbide in air.

2. Experimental details*

SiC whiskers from Tokai were placed in alumina crucibles and heated in air for 0.5, 1.0, 2.0 or 4.0 h at 600, 700 or 800 °C. A Leco furnace Model 542-27 with an Omega Model CN 2011 K temperature controller was used. The temperature regulation is ± 2 °C.

Samples were prepared for XPS analysis by sprinkling the treated whiskers on adhesive tape so as to achieve uniform and complete coverage. The XPS data were obtained with a modified AEI ES-100 photoelectron spectrometer. This instrument uses a magnesium X-ray source. Data collection on the XPS instrument was accomplished with a Motorola 68000-based microprocessor which was interfaced to a

*Certain commercial equipment, instruments, or materials are identified in this paper in order to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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VAX11/780 minicomputer. Data processing was done using custom software which includes published algorithms for fast Fourier transform (FFT) smoothing and for peak-stripping based on the Levenberg–Marquardt non-linear least-squares method [8].

3. Results and discussion

Fig. 1 shows the C1s scan of the as-received SiC whiskers. The peaks at binding energies of 282.9, 284.8 and 286.5 eV can be identified to be from SiC, free carbon or hydrocarbon and C–O, respectively. The Si2p spectra from the as-received SiC whiskers as well as from SiC samples heated at 700 °C for 0.5, 1.0, 2.0 and 4.0 h are shown in Fig. 2. The Si2p peaks from SiO_2 and SiC are at 102.9 and 100.3 eV, respectively. Note that this figure shows that the SiO_2 intensity from the oxide layer on the surface of the SiC whiskers increases with increasing oxidation time.

From the ratio of the Si2p intensities from SiC and SiO_2 the thickness of SiO_2 overlayers can be determined as a function of heating time and temperature. From the work of Carlson and McGuire [9], if R is the ratio of the SiC 2p intensity to the SiO_2 2p intensity then we have

$$R = R^* \left(\frac{e^{-t/\lambda}}{1 - e^{-t/\lambda}} \right) \quad (1)$$

where t is the SiO_2 layer thickness, λ is the inelastic mean free path of the the Si2p photoelectron and R^* is the 2p ratio of the pure SiC to the completely oxidized SiC. Equation 1 can be solved in terms of the SiO_2 layer thickness to give

$$t = -\lambda \ln \left(\frac{R}{R + R^*} \right) \quad (2)$$

The oxide layer thickness can also be written in terms of I_0, the SiO_2 intensity, as

$$t = -\lambda \ln \left(1 - \frac{I_0}{I_0^*} \right) \quad (3)$$

where I_0^* is the SiO_2 2p intensity from a completely oxidized sample, or in terms of the SiC intensity, I_c, as

$$t = -\lambda \ln (I_c / I_c^*) \quad (4)$$

where I_c^* is the SiC intensity from a sample with no surface oxide. Direct measurements of the values of I_0^*, I_c^* and R^* are complicated by the difficulty in preparing completely oxidized SiC samples and SiC samples with no surface oxide. These values, however, can be obtained indirectly. Solving between Equations 3 and 4 gives

$$\frac{I_c}{I_c^*} = 1 - \left(\frac{I_0}{I_0^*} \right) \quad (5)$$

This implies that the SiC intensity, I_c, will be a linear function of the SiO_2 intensity, I_0. The values of I_0^* and I_c^* can then be obtained from the x- and y-intercepts in a plot of SiC intensity against SiO_2 intensity. Fig. 3 shows this plot for the 13 samples analysed in this

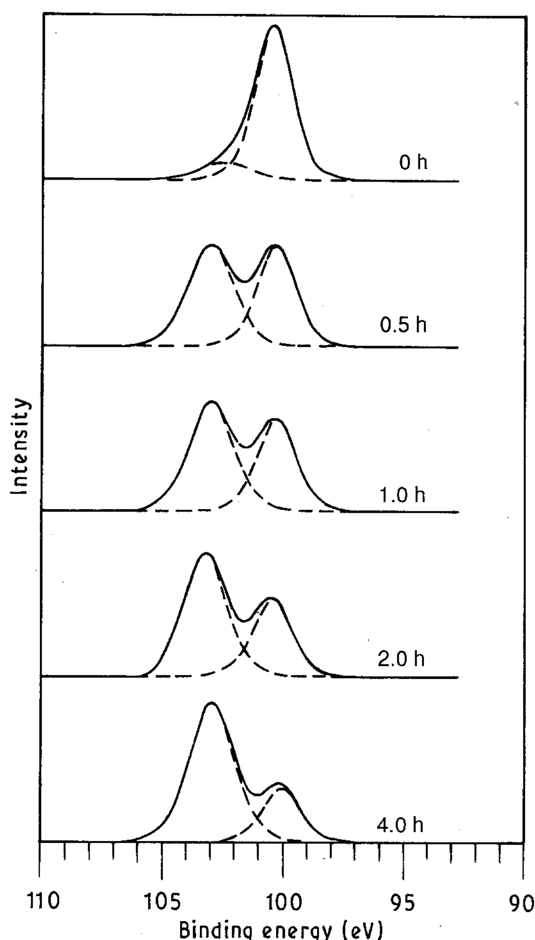

Figure 2 Si2p XPS spectra of SiC whisker samples heated in air at 700 °C.

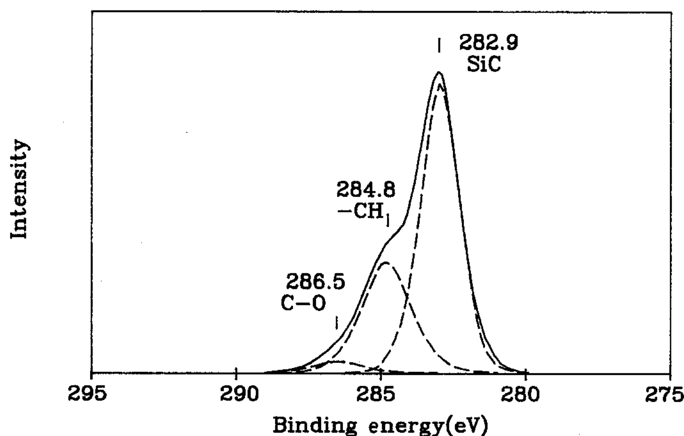

Figure 1 C1s XPS spectrum of an as-received SiC whisker sample.

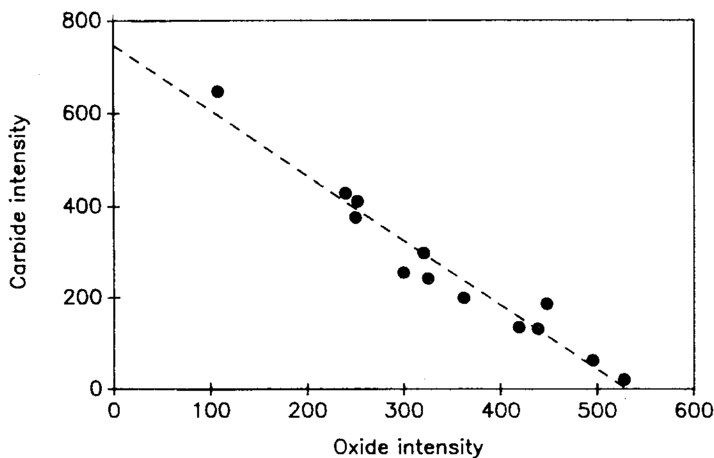

Figure 3 SiC and SiO_2 Si2p XPS peak intensities.

TABLE I Measured oxide thickness on SiC whiskers heated in air at 600 to 800 °C

Time (h)	Temperature (°C)	t (nm)	δt (nm)
0.5	600	1.68	0.22
1.0	600	1.80	0.23
2.0	600	1.92	0.24
4.0	600	2.67	0.26
0.5	700	2.83	0.32
1.0	700	3.07	0.33
2.0	700	3.66	0.36
4.0	700	4.86	0.42
0.5	800	4.24	0.40
1.0	800	5.01	0.43
2.0	800	7.03	0.51
4.0	800	10.37	0.68
0	Unheated	0.61	0.11

study. The least-squares fit to this data gives

$$I_c = -(1.39 \pm 0.07)\, I_0 + (745 \pm 21) \quad (6)$$

From Equation 6, the value of $R^* = I_c^*/I_0^*$ was determined to be 1.39 ± 0.17.

The oxide layer thickness on the SiC whiskers has been determined from Equation 2 for each heating time and temperature. The value of λ was determined from the data of Powell [10] to be 2.9 nm. The error in a particular thickness measurement, δt, can be determined by differentiating Equation 2 to give

$$\delta t = -\lambda\left(\frac{R^*}{R + R^*}\right)\frac{\delta R}{R} \pm \lambda\left(\frac{1}{R + R^*}\right)\delta R^* \quad (7)$$

The value of $\delta R/R$ is determined from the Poisson noise in each spectrum and the value of δR^* was determined from Equation 6 to be 0.17. Table I gives the measured values of t and δt. The values of t have then been plotted in Fig. 4.

For each of the three temperatures, the least-squares linear fits to the data gave correlation coefficients greater than 0.98, which is indicative of the good agreement. The equations for the SiO_2 layer thickness, t, are then given by:

$$600\,^{\circ}\mathrm{C}:\ t = (0.282 \pm 0.040)h + (1.49 \pm 0.09) \quad (8)$$

$$700\,^{\circ}\mathrm{C}:\ t = (0.585 \pm 0.011)h + (2.51 \pm 0.03) \quad (9)$$

$$800\,^{\circ}\mathrm{C}:\ t = (1.767 \pm 0.051)h + (3.35 \pm 0.12) \quad (10)$$

where h is the heating time in hours. The linear rate constants are then given by the slopes of these three lines and are plotted in Fig. 5 in an Arrhenius-type plot. The activation energy can then be determined from this plot to be 17.2 ± 2.8 kcal mol^{-1} (72 ± 12 kJ mol^{-1}). This value is somewhat lower than the value of 26 kcal mol^{-1} (109 kJ mol^{-1}) that Suzuki *et al.* [11] obtained for linear oxidation of the $(000\bar{1})$ carbon face of SiC in the oxygen between 850 and 1100 °C. It should be mentioned, however, that

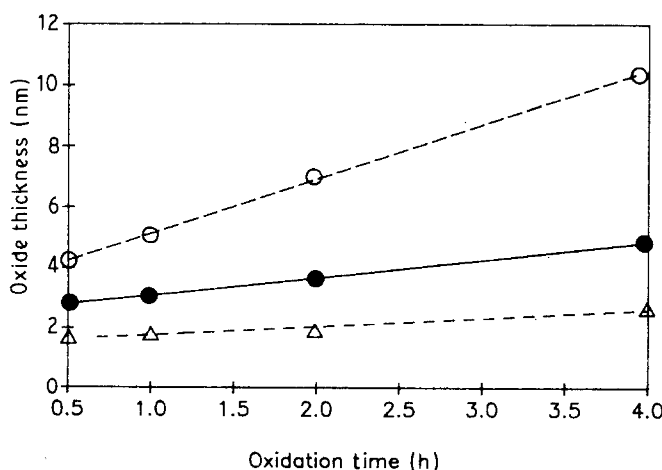

Figure 4 Surface oxide film growth on SiC whisker in air: (△) 600 °C, (●) 700 °C, (○) 800 °C.

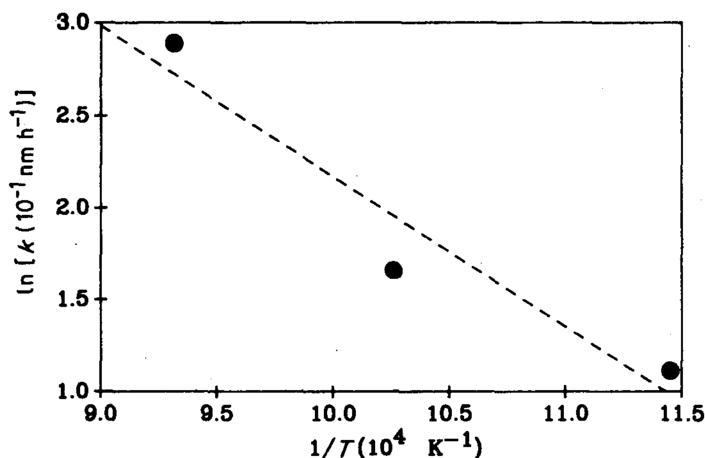

Figure 5 Rate constants against $1/T$ for SiC whiskers heated in air.

the oxidation rates measured for these whiskers will be a composite of the rates for all of the various crystal faces.

4. Conclusions

XPS has been used to study the growth of SiO_2 layers on SiC whiskers heated in air at temperature of 600, 700 and 800 °C. The thicknesses of these layers were determined from the Si2p intensities from SiC and SiO_2. The uncertainties in these thickness measurements were also calculated. Oxidation at each of these three temperatures was found to follow a linear rate law. This is in accordance with previous predictions since, for very thin oxide layers, the surface chemical reaction will be the dominant rate-determining step. An activation energy for linear oxidation in this temperature range has been calculated.

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