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Oxidation kinetics of hot-pressed silicon carbide

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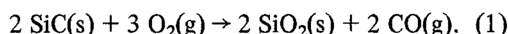
The oxidation of silicon carbide, hot-pressed with ~ 4 wt % Al_2O_3, in 1 atm dry oxygen follows classical parabolic behaviour with an activation energy of 481 kJ mol^{-1} in the temperature range 1200 to 1400° C. The oxide film consists predominantly of cristobalite and a glassy phase in which additive (Al) and various impurity elements (Fe, Na, K, etc) concentrate. The desorption of CO(g) from the SiC/SiO_2 interface appears to be oxidation rate controlling.

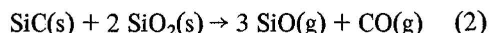
1. Introduction
High-strength, hot-pressed silicon carbide has attracted great attention in recent years because of its possible use for high temperature structural applications in demanding environments [1, 2]. A great deal of effort has been devoted to the development of fabrication techniques [3–5], and in studying its physical and mechanical properties [6]. Although extensive studies [7–14] have been carried out in the past on the oxidation of powdered and chemically vapour-deposited SiC, very little is known regarding the oxidation behaviour of dense SiC hot-pressed with the aid of additives.

At high temperatures, SiC exhibits two types of oxidation behaviour, "active" and "passive", depending upon the ambient oxygen potential [13, 14]. At high oxygen pressures, "passive" oxidation occurs wherein a protective film of SiO_2(s) is formed on the surface by the reaction:



$$2\ SiC(s) + 3\ O_2(g) \rightarrow 2\ SiO_2(s) + 2\ CO(g). \quad (1)$$

At low oxygen potentials, severe "active" oxidation occurs due to the formation of gaseous products according to reactions:



$$SiC(s) + 2\ SiO_2(s) \rightarrow 3\ SiO(g) + CO(g) \quad (2)$$

$$SiC(s) + O_2(s) \rightarrow SiO(g) + CO(g). \quad (3)$$

However, Gulbransen and Jansson [14] have shown that this active oxidation of SiC occurs only at oxygen pressures lower than $\sim 3 \times 10^{-4}$ atm at 1400° C. The purpose of this paper is to report only on the "passive" oxidation behaviour of commercially available hot-pressed SiC in 1 atm oxygen in the temperature range 1000 to 1400° C.

2. Experimental
2.1. Material
Silicon carbide used in this study was commercially* prepared by hot-pressing SiC powder with about 4 wt % Al_2O_3, and was obtained in the form of ~ 2.5 cm thick billets. The chemical analysis of the material is shown in Table I. In addition to Al_2O_3, the material contained minor amounts of Fe, Ti, Ca, Cr, Na, K, etc. The material also contained ~ 4 wt % tungsten in the form of tungsten carbide, which gets entrapped during prolonged ball milling of starting powders with tungsten carbide media.

The X-ray diffraction analysis identified several

TABLE I Emission spectrographic analysis of SiC

Element	wt %
Al	1.0
Fe	0.1
Ti	0.03
Ca	0.01
Cr	0.01
Ni	0.005
Mg	0.001
Na	0.001
K	0.001
W	~ 4

* Grade NC-203, Norton Company, Worcester, MA.

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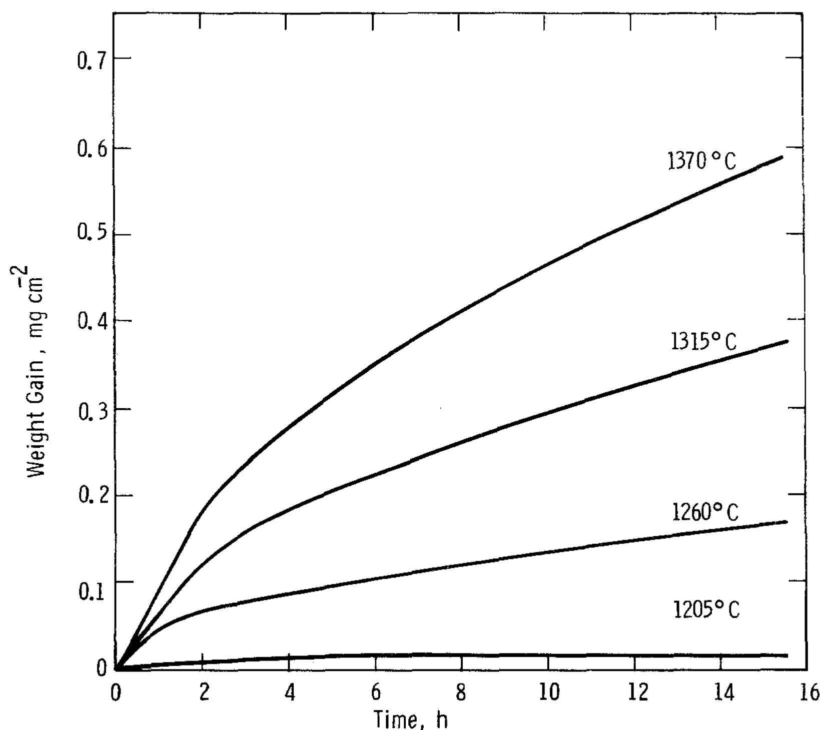

Figure 1 Weight change versus time curves for oxidation of hot-pressed SiC in dry oxygen at 1 atm pressure.

polymorphs of SiC (6H major, 4H minor, 15R and 21R traces) and WC as the only phases present in the starting material. Alumina was not detected in the starting material by powder X-ray diffraction indicating that it is either not present in free form in sufficient quantity, or more probably, that it is present as a constituent of an amorphous phase in the grain boundaries.

2.2. Experimental procedure

The silicon carbide specimens, in the form of 1 cm x 1 cm and 0.2 cm thick plates, were cut from the hot-pressed billets, and polished with up to 6 μm diamond paste. The polished and cleaned specimen was suspended from one end of an automatic electrobalance† and held inside an alumina reaction tube at the desired temperature. The changes in the weight of the specimen were continuously recorded on a strip chart recorder.

The oxidation experiments were performed in dry oxygen at 1 atm pressure (1.01 x 10^5 Pa). The oxygen gas was dried by passing through anhydrous calcium sulphate and phosphorous pentoxide before being passed over the specimen in the reaction tube.

After oxidation at different temperatures, the surface of the specimens were analysed by X-ray diffraction, scanning electron microscopy, electron microprobe analysis and ion probe mass spectrometry to characterize completely the oxidation products.

3. Results

3.1. Oxidation kinetics

As SiC oxidizes to SiO_2 according to Reaction 1, the difference in the molecular weights of SiC (40 g mol^{-1}) and SiO_2 (60 g mol^{-1}) is reflected as weight gain during oxidation. These weight gain data for oxidation of SiC in 1 atm dry oxygen at different temperatures are summarized in Fig. 1. The weight gained at and below 1200° C was insignificant. The weight gain versus time curves at all temperatures approximate the classical parabolic behaviour after about 1 to 2 h from the start of oxidation. This parabolic behaviour can be represented by the equation:

$$W^2 = K_p \cdot t$$

where W is the weight gain in time t, and K_p is the parabolic rate constant. Fig. 2 shows square of the weight gain (W^2) plotted as a function of time (t) for different temperatures of oxidation. The

† Cahn Instruments Division, Ventron Corp, Cerritos, CA.

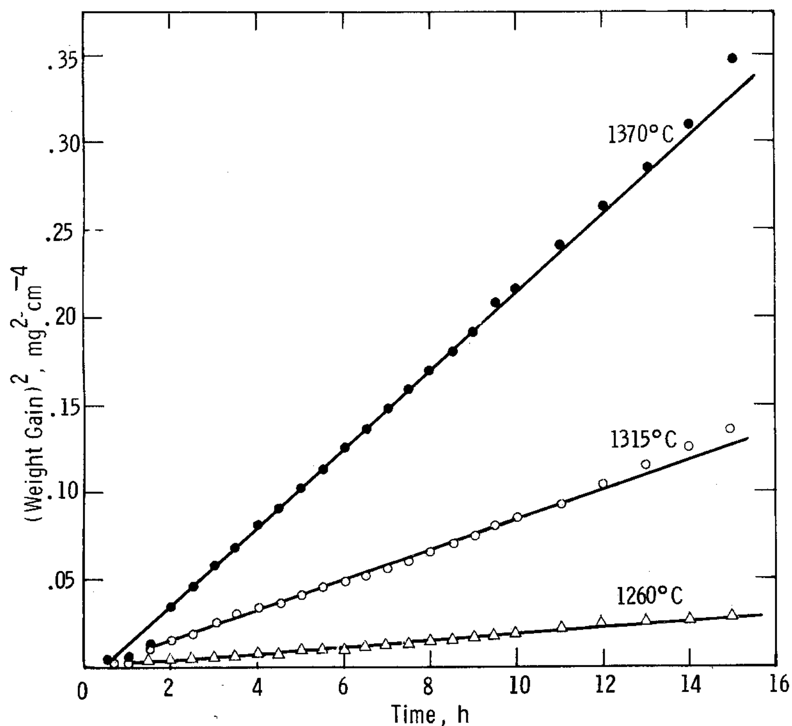

Figure 2 Parabolic plots for oxidation of hot-pressed SiC in dry oxygen at 1 atm pressure.

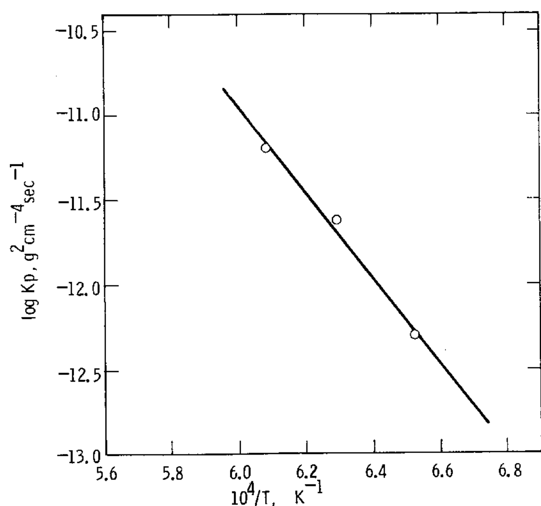

Figure 3 Parabolic rate constants for oxidation of hot-pressed SiC in oxygen at 1 atm pressure as a function of temperature.

straight lines represent regions of parabolic oxidation behaviour at each temperature. The parabolic rate constants (K_p), obtained from the slopes of these straight lines, are shown as a function of reciprocal temperature in Fig. 3. Using the Arrhenius equation:

$$K_p = A \exp(-E/RT)$$

where E is the activation energy, R the gas constant, and T the absolute temperature, an activation energy of 481 kJ mol^{-1} is obtained for the oxidation of hot-pressed SiC in 1 atm dry oxygen.

The weight gained during the first 1 to 2 h oxidation was somewhat less than the parabolic rate observed after this initial oxidation. As mentioned earlier, the hot-pressed SiC used in this study contained about 4 wt% tungsten carbide. During initial oxidation, the tungsten carbide on the surface of the SiC specimen oxidizes to either solid tungsten oxides with very high vapour pressures, or to various volatile tungsten oxides, causing a small loss in weight. This loss in weight causes the initial weight gain obtained in oxidizing SiC to be somewhat less than the weight gain expected from the parabolic rate observed after this initial period.

3.2. Characterization of oxidation products

The X-ray diffraction analyses of the oxide formed on SiC at temperatures from 1093 to 1370° C revealed the presence of mostly cristobalite (SiO_2) with substantial amounts of a glassy phase. No alumina or aluminium silicate was identified in oxide formed up to 1260° C, but small traces of aluminium silicate ($3\,Al_2O_3 \cdot 2\,SiO_2$) were observed in oxide formed at 1315 and 1370° C. There was no evidence of any tungsten oxides in the X-ray patterns, indicating that either their concentration was too low to be detected by X-ray diffraction,

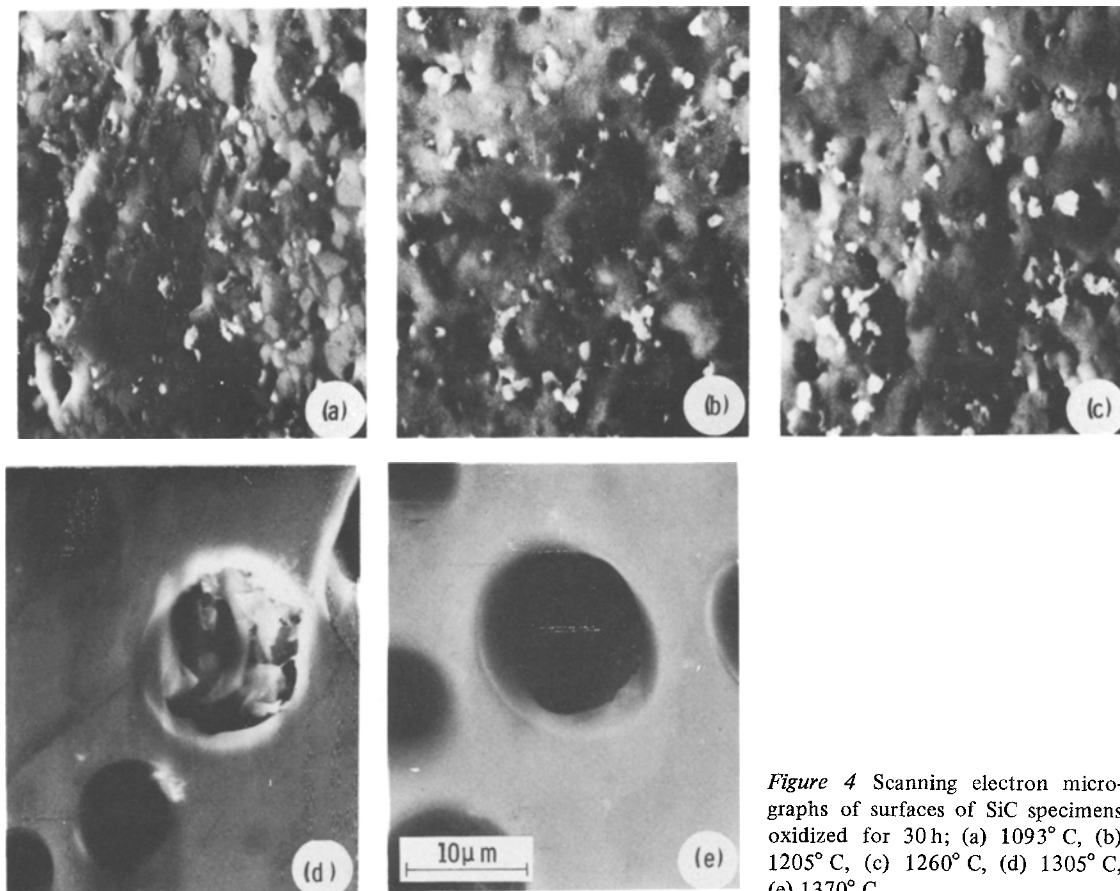

Figure 4 Scanning electron micrographs of surfaces of SiC specimens oxidized for 30 h; (a) 1093° C, (b) 1205° C, (c) 1260° C, (d) 1305° C, (e) 1370° C.

or they were formed in the gaseous state.

The surface morphologies of the oxide films formed on SiC after oxidation in dry oxygen for 30 h at various temperatures are shown in the scanning electron micrographs in Fig. 4. At 1093° C, very little oxide was formed which left the underlying SiC grain structure still visible after 30 h of oxidation. At oxidation temperatures of 1205 and 1260° C, the surface was covered with a layer of cristobalite and a glassy phase with small white particles distributed throughout the surface. These white particles were inferred to be aluminium silicate by energy dispersive X-ray analysis. At oxidation temperatures of 1315 and 1370° C, the surface was uniformly covered with a smooth oxide layer which appeared to have been liquid at the oxidation temperature, and no discrete alumina particles were observed on it. The oxide layers at these temperatures were full of tiny pores which were apparently formed at the oxidation temperature by the escape of gaseous oxidation products from the SiC/SiO_2 interface.

The scanning electron micrograph of the transverse section of an oxidized SiC specimen is shown in Fig. 5 along with the energy dispersive X-ray analysis both in the SiC substrate and in the oxide layer thereon. While only Si peak was detected in the SiC substrate, Al, K and Fe peaks were also present in the scan on the oxide film.* These elements must, therefore, diffuse outwards during the oxidation process to concentrate in the oxide film. The presence of these elements in the oxide was also confirmed by the electron microprobe analysis of the oxide film. The microprobe traces for Si, Al, O and K through the oxide layer are shown in Fig. 6, which clearly indicate that Al and K are present in the oxide in much greater quantities than in the SiC substrate.

The oxide layer was further analysed by a Cameca ion probe mass spectrometer, where a SiC specimen oxidized at 1370° C for 24 h was bombarded with an oxygen primary beam and the

* The Au and Pd peaks in the scan are from the surface film of an Au–Pd alloy deposited on oxidized SiC specimen to obtain a conducting surface.

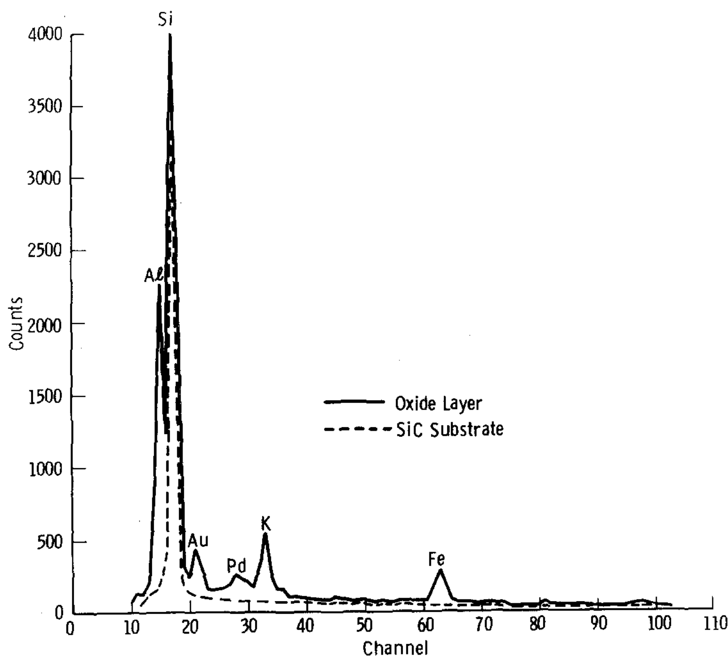

Figure 5 Scanning electron micrograph of the transverse section of a SiC specimen oxidized at 1370° C for 1203 h with energy dispersive X-ray analysis in the oxide layer and in the SiC substrate.

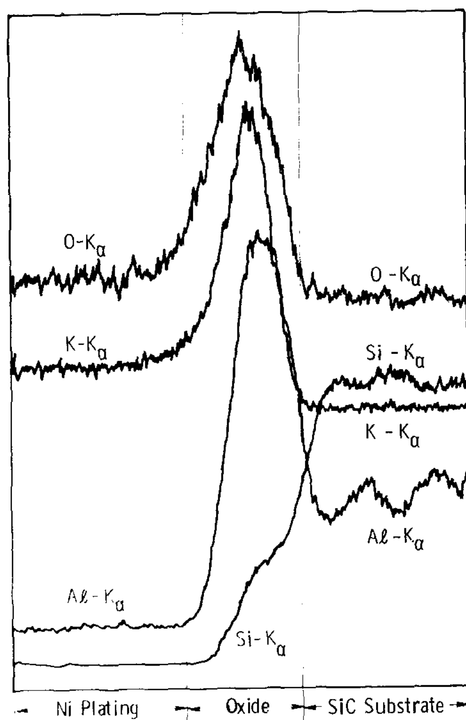

Figure 6 Electron microprobe traces through the oxide film on a SiC specimen oxidized for 4000 h at 1370° C.

identity of the secondary ions arising from the surface of the oxide was determined by mass spectrometric analysis. The ion images for Si, O, Al, W, Na and K from a single region of the oxide are shown in Fig. 7, further confirming the presence of impurity elements in the oxide film. The concentration profiles for W, Al and O obtained by ion probe mass spectrometric analysis, Fig. 8, show that Al is present in the oxide in much greater quantity than in SiC itself. However, the concentration of tungsten in the oxide is less than in the SiC substrate, further indicating that some tungsten might have been lost from the surface during oxidation as volatile oxides.

4. Discussion

4.1. Effect of additive and impurity elements

The existence of cristobalite at a temperature of 1093° C suggests that additive (Al_2O_3) and impurity elements (Fe, K, etc) lower the devitrification temperature of silica glass by reducing its viscosity [15]. The presence of appreciable amounts of Fe and K in the oxide layer could also explain the formation of a liquid oxide at as low a

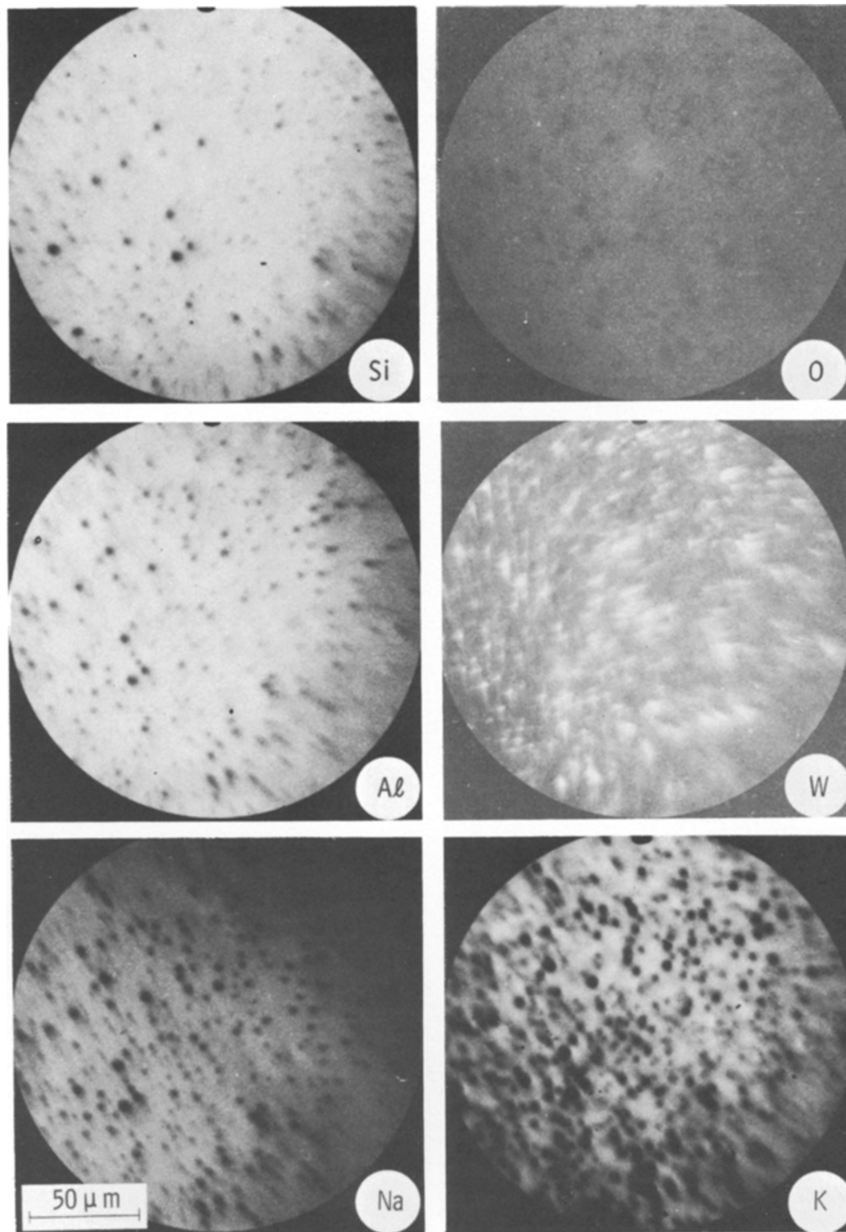

Figure 7 Ion images from a single region of the oxide on a SiC specimen oxidized for 24 h at 1370° C.

temperture as 1315° C, since a liquid phase should not be formed by the reaction between SiO_2 and Al_2O_3 only until ~ 1600° C [16]. Thus these additive and impurity elements control the nature of the surface layer formed on oxidation, and this results in a very different oxidation rate for hot-pressed SiC as compared to that of pure SiC (e.g. CVD–SiC). The different concentrations of additive and impurity elements can cause different rates of oxidation by forming oxides of differing viscosities, since the gaseous diffusion is inversely related to the viscosity of the oxide in accordance with Stokes–Einstein relationship. It has been confirmed experimentally that the oxidation rates of SiC materials hot-pressed with different additives (e.g. Al_2O_3 and B), and with varying amounts of the same additive (Al_2O_3) are widely different [6, 17]. Thus the oxidation behaviour of hot-pressed

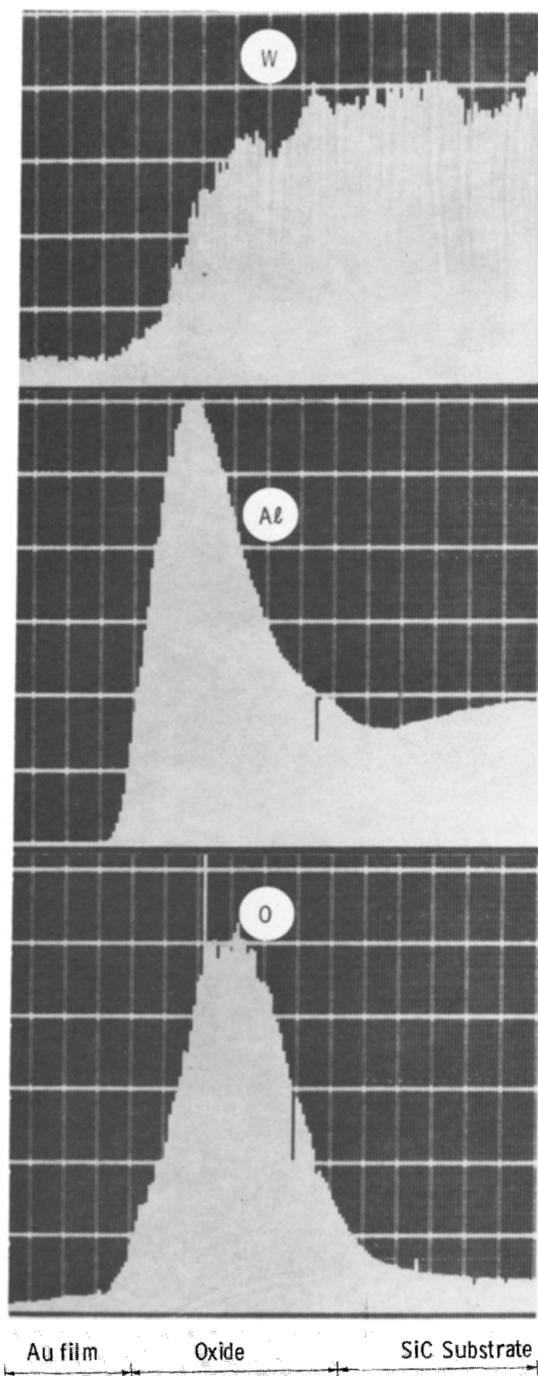

Figure 8 Concentration profiles across the oxide layer on a SiC specimen oxidized for 24 h at 1370° C.

SiC is determined predominantly by the nature and concentration of the hot-pressing additives and the impurity elements rather than by the intrinsic oxidation of SiC to SiO_2.

4.2. Processes occurring during oxidation

The parabolic nature of the rate curves indicate that the oxidation of hot-pressed SiC is controlled by a diffusional mechanism. It has been suggested by various authors [7–10] that the growth of the oxide layer on SiC occurs by the inward diffusion of oxygen ions or molecules, with an activation energy in the range 65 to 277 kJ mol^{-1}. Even though there is a wide variation in these literature values of the activation energy (presumably due to the formation of silica in either crystalline or amorphous form), oxygen transport as the rate controlling step in the oxidation of hot-pressed SiC seems unlikely in view of the high value of the activation energy, 481 kJ mol^{-1}, obtained in the present investigation. However, high values of activation energy in the range 405 to 548 kJ mol^{-1} have also been reported by Pultz and Hertl [18] for CO(g) desorption from the SiC/SiO_2 interface in the temperature range 1270 to 1430° C. Pultz [12] also studied the oxidation of particulate SiC in O_2 and O_2–He gas mixtures and obtained an activation energy of 632 kJ mol^{-1} in the temperature range 1335 to 1445° C. In view of these results, it appears that in the oxidation of hot-pressed SiC, the desorption of CO(g) from the SiC/SiO_2 interface is the rate controlling process. The small differences in the values of the activation energy in these investigations may be either due to very high sensitivity of activation energy to temperature ranges, or due to differing viscosities of the oxide layer formed. The evolution of CO(g) causes the formation of a pore network in the oxide layer as observed in the scanning electron micrograph in Fig. 4.

During the oxidation of SiC, SiO(g) is also formed at the SiC/SiO_2 interface according to Reaction 2. However, at temperatures up to 1400° C, the equilibrium partial pressures of SiO(g) thus formed are not appreciable [14]. Any SiO(g) formed at the interface should, however, be oxidized to SiO_2(s) by reaction with oxygen gas in pores and fissures in the oxide layer.

5. Conclusions

(1) The oxidation of hot-pressed SiC in 1 atm dry oxygen follows classical parabolic behaviour with an activation energy of 481 kJ mol^{-1} in the temperature range 1200 to 1400° C.

(2) The desorption of CO(g) from the SiC/SiO_2 interface appears to be the rate controlling process.

(3) The oxide film formed consists mostly of cristobalite with a glassy phase in which additive (Al) and impurity elements (Fe, K, Na, etc) concentrate.

(4) The additive and the impurity elements affect the viscosity of the oxide formed, and thus affect the oxidation rate.

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