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Passive Oxidation of an Effluent System: The Case of Polymer-Derived SiCO

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The oxidation kinetics of non-oxides depend on the inward diffusion of oxygen from the environment through the passivating silica overgrowth, the outward diffusion of the effluent species, e.g., CO, produced by the oxidation reaction at the interface, and the chemical driving forces for diffusion. An analysis that combines these factors into a unified theory is presented. The analysis is applied to experiments on the oxidation of polymer-derived amorphous silicon oxycarbide (SiCO) ceramics containing different amounts of carbon. The comparison between theory and experiment suggests that the activity of the so-called "free carbon" in SiCO is likely to be less than unity, which explains why the oxidation of SiCO is passive in nature. Further, the analysis provides quantitative answers to the following questions: (a) How is the effective diffusivity for the parabolic rate constant related to the composition of the substrate, the inward diffusivity of oxygen, and the outward diffusivity of CO? (b) How does the rate constant depend on the activity of carbon in the substrate *and* on the activity of carbon in the environment? (c) How is the pressure of CO generated at the interface related to the carbon activity and the diffusion coefficients? The analysis points towards the need for systematic experiments in controlled O_2/CO_2 environments for a more complete understanding of the oxidation kinetics of carbon-based ceramics.

I. Nomenclature

The parameters in the analysis fall into four categories. The first set is related to the composition of the substrate and the parameters that are determined by the composition, such as the relative rates of O_2 and CO fluxes that must be constrained by mass balance. The density, the molecular weight, and the thickness of the passivation overgrowth, and the same for the substrate also fall in this category.

Parameters related to composition and geometry:

x,y	defines the composition of the substrate: as in SiC_xO_y
α	mole of SiO_2 produced at the interface for one mole O_2 diffusing from the surface
f	a parameter related to composition that ensures mass balance
χ_C	the molar concentration of carbon in SiC_xO_y
Mw_{silica}	molecular weight of silica
Mw_{SiCO}	molecular weight of SiC_xO_y (per one silicon basis)
ρ_{silica}, ρ_{SiCO}	densities of silica and SiC_xO_y
h, or h_{silica}	the thickness of the silica overgrowth ($h_{silica} = h$, as defined above)
z_{SiCO}	the recession rate of the substrate
V_{SiO_2}	molar volume of SiO_2, the overgrowth

The next two categories of symbols are related to the definition of the thermodynamic quantities. These are separated into two groups, the first referring to the silica–substrate interface, and the other to the silica–air interface. We faced the prospect of a complicated symbol-structure to distinguish between the activities of the various constituents at these two interfaces (e.g., the activity of oxygen would require subscript of O_2 as well as a superscript of "i", for example to distinguish one interfacial activity from the other). At the risk of being strident, we have chosen to use Roman letters to denote the activity at the atmospheric interface and Greek symbols to denote the thermodynamic parameters for the silica-substrate interface. Thus, activity of carbon in the atmosphere is written as a_C, but at the buried interface it is written as φ_C. Similarly, the partial pressure of CO in the atmosphere is p_{CO}, but at the silica-substrate interface it is written as π_{CO}.

Thermodynamic parameters for the atmosphere/SiO_2 interface:

p_{O_2}, p_{CO}, p_{CO_2}	partial pressure of gas species in the environments
ΔG_{CO_2}	free energy for the reaction $C+O_2=CO_2$ (kJ/mol)
a_C	activity of carbon in the environment

Thermodynamic parameters at the SiO_2/SiC_xO_y interface

π_{O_2}, π_{CO}	the activities (that is, that partial pressure) of O_2 and CO at the interface
ϕ_C	activity of carbon in the substrate
ΔG_{CO}	free energy for the reaction $C+\frac{1}{2}O_2=CO$ (kJ/mol)
γ_C	the activity coefficient for carbon for Henry's law Eq. (18).

The final set of parameters is related to the kinetics of the oxidation reaction. The reaction is assumed to be controlled by the inward and outward diffusion of O_2 and CO, respectively, through the passivation overgrowth. Thus most parameters listed below pertain to the basic equation for diffusion that related

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the flux to the diffusion coefficient, the molar concentration of the diffusing species in the medium, and the driving force for diffusion expressed as the difference between the chemical potential on the two sides of the overgrowth. Finally, the parabolic rate constant is given the subscript "xp" to emphasize that it represents the phenomenological measurement of the parabolic oxidation behavior. The mission of the analysis was to relate k_{xp} to the fundamental thermodynamic and kinetic parameters, such as activities of the constituents and their diffusivities through the silica overgrowth. This result is finally achieved in Eq. (16).

Kinetic parameters related to diffusion and oxidation rate:

J_{CO}	flux of CO molecules (mol/m$^2\cdot$s) from interface to the surface
J_{O_2}	flux of O_2 molecules (mol/m$^2\cdot$s) from surface to the interfaces
D_{O_2}	diffusion coefficient for O_2 through SiO_2 (m^2/s)
D_{CO}	diffusion coefficient for CO molecules through SiO_2 (m^2/s)
n_{CO}	molar concentration CO in SiO_2
$\Delta\mu_{O_2}, \Delta\mu_{CO}$	chemical potential difference between the interface and the surface
λ	ratio of composition corrected permeabilities of CO_2 and CO
D_{eff}	the effective diffusion coefficient for the oxidation process
k_{xp}	phenomenological parabolic rate constant

II. Introduction

Polymer-derived ceramics (PDCs) are predominantly amorphous materials obtained from controlled pyrolysis of highly cross-linked polymers. Two systems have been studied: SiCN, made from polysilazanes,[1] and silicon oxycarbide (SiCO), made from silseaquioxanes[2]. A characteristic feature of these materials is the incorporation of excess, or "free" carbon relative to compositions corresponding to the stoichiometric mixtures of silicon carbide (SiC) and Si_3 N_4 or SiC and SiO_2.[3] Recent work on SiCN ceramics has shown that despite the presence of excess carbon, their oxidation behavior is passive,[4] like that of SiC and Si_3N_4.[5,6] A detailed comparison of the parabolic rate constants has shown that SiCN oxidizes at approximately the same rate as CVD silicon nitride and silicon carbide.[7,8] These results demonstrate that the carbon activity in SiCN, despite its amorphous character,[1] is fairly low, comparable to the activity of carbon in crystalline SiC.

In contrast to SiCN, oxidation studies in the SiCO system have been rare. To our knowledge, the present work is the first of its kind, although oxidation of SiCNO fibers has been reported.[9] The study of SiCO is particularly interesting because, unlike SiCN, the precursors for SiCO can be chosen to vary the carbon content, and therefore its activity, over a wide range (the range for the present experiments is given in Fig. 1). For example, among other questions listed in the Abstract, we were interested to see if, beyond a certain activity of carbon, it was possible to observe an *incipient* transition from passive to active oxidation.[4,10] The paper begins with a detailed analysis that can provide insights into the relationship between the activity of carbon in the substrate and the oxidation behavior. The results of the oxidation experiments are then analyzed within the scope of these theoretical results.

III. Theory

The parameters in the analysis are defined under Nomenclature.

As shown schematically in Fig. 2, we consider the growth of the SiO_2 overlayer to take place by the diffusion of oxygen from the atmosphere to the interface. The reaction among oxygen, silicon, and carbon at the interface is expected to produce CO[11] that must diffuse back out to the free surface. The *two principal unknowns* in the coupled diffusion problem are the partial pressure of oxygen, and that of carbon monoxide, at the interface. We call them π_{O_2} and π_{CO}, respectively, using the symbol π to denote the partial pressures at the interface. The partial pressures of CO_2 and O_2 in the environment are written with Roman symbols, p_{CO_2} and p_{O_2}. The activity of carbon at the interface is called φ_C, again using the Greek symbol to define the thermodynamic quantities at the interface (the activity of carbon in the environment is written as a_C). The coefficients of diffusion for O_2 and CO through the silica overlayer are called D_{O_2} and D_{CO}. The permeation constant for the transport of CO through silica is then given by $D_{CO}n_{CO}$, where n_{CO} is the molar solubility of CO. The transport equations for O_2 and CO through the silica overgrowth can be written down immediately as follows:

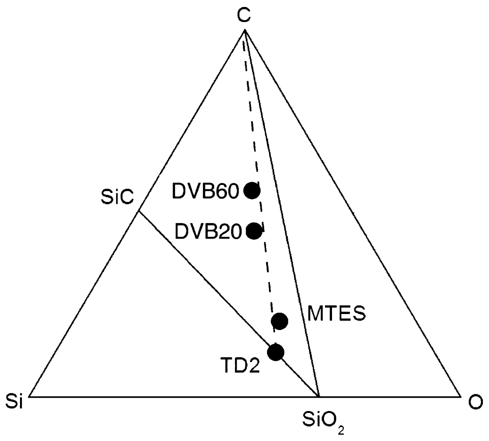

Fig. 1. The composition of the four samples.

$$J_{O_2} = \frac{D_{O_2}}{V_{SiO_2}RT}\frac{\Delta\mu_{O_2}}{h} \tag{1}$$

and

$$J_{CO} = \frac{D_{CO}n_{CO}}{V_{SiO_2}RT}\frac{\Delta\mu_{CO}}{h} \tag{2}$$

where

$$\Delta\mu_{CO} = RT\ln\frac{\pi_{CO}}{p_{CO}} \quad \text{and} \quad \Delta\mu_{O_2} = RT\ln\frac{p_{O_2}}{\pi_{O_2}} \tag{3}$$

Here, J is the flux of the species denoted by the subscript in units of moles per unit area per unit time. Similarly, $\Delta\mu$ is the chemical potential difference for each species between the free surface and the interface. The molar volume of silica is given by V_{SiO_2}. The

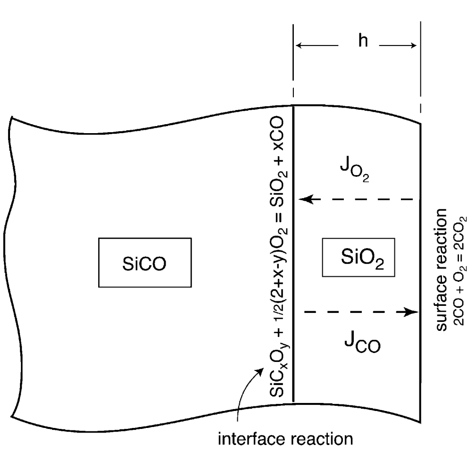

Fig. 2. The couples diffusion problem in passive oxidation of an effluent system. The carbon monoxide evolved at the interface must diffuse out just as the oxygen diffuses toward the interface.

thickness of the overgrowth is h, and RT is the gas constant times the temperature in degrees K.

Now, the magnitudes of the two fluxes are constrained by the oxidation reaction taking place at the interface where oxygen reacts with SiC_xO_y to produce carbon monoxide:

$$SiC_xO_y + \frac{2+x-y}{2}O_2 = SiO_2 + xCO \tag{4}$$

Since x moles of CO are produced for $(2+x-y)/2$ moles of oxygen diffusing to the interface from the environment, the fluxes are related to one another by the following equation:

$$J_{O_2} = fJ_{CO} \tag{5}$$

where

$$f = \frac{2+x-y}{2x} \tag{6}$$

The substitution of Eqs. (1) and (2) into Eq. (5) leads to the following result:

$$\ln\left(\frac{p_{O_2}}{\pi_{O_2}}\right) = \lambda \ln\left(\frac{\pi_{CO}}{p_{CO}}\right) \tag{7}$$

where

$$\lambda = \frac{fD_{CO}n_{CO}}{2D_{O_2}} \tag{8}$$

Equation (7) gives one of the two relationships required to solve for the two unknowns, the activity of O_2 and CO, that is their partial pressure, at the interface. The other equation is obtained by enforcing equilibrium between the activities of carbon and oxygen as controlled by the following reaction:

$$C + \frac{1}{2}O_2 = CO \tag{9}$$

Equation (9) must hold both at the free surface and at the interface. By enforcing chemical equilibrium at both sites, we write that:

$$e^{-\Delta G_{CO}/RT} = \frac{p_{CO}}{p_{O_2}^{1/2} a_C} = \frac{\pi_{CO}}{\pi_{O_2}^{1/2} \phi_C} \tag{10}$$

where ΔG_{CO} is the free energy for the reaction in Eq. (9) from the standard states of the constituents. The Roman symbols describe the partial pressures and the activity of carbon at the free surface, while the Greek symbols are used for the interface.

Combining the right-hand side in Eq. (10) with Eq. (7) leads to the solution for the interfacial pressures of O_2 and CO:

$$\ln\left(\frac{p_{O_2}}{\pi_{O_2}}\right) = \frac{2\lambda}{1+\lambda} \ln\left(\frac{\phi_C}{a_C}\right) \tag{11}$$

$$\ln\left(\frac{\pi_{CO}}{p_{CO}}\right) = \frac{1}{1+\lambda} \ln\left(\frac{\phi_C}{a_C}\right) \tag{12}$$

The problem is now solved. For example, the flux of oxygen can be calculated by inserting Eq. (11) into Eq. (1).

It now remains to obtain an expression for the parabolic rate constant obtained by measuring the growth rate of the overlayer, defined as follows:[12]

$$h^2 = k_{xp}t \tag{13}$$

Here h is the thickness of the overgrowth with time, t. The rate constant, k_{xp}, is given the subscript "xp" to highlight its phenomenological nature. The rate of growth is related to the flux of oxygen by using mass conservation:

$$\frac{dh}{dt} = \frac{1}{\alpha} J_{O_2} V_{SiO_2} \tag{14}$$

where

$$\alpha = \frac{2+x-y}{2} \tag{15}$$

since, from Eq. (4), α moles of oxygen diffusing from the environment to the interface will produce one mole of silica. Substituting for J_{O_2} from above into Eq. (14), differentiating Eq. (13) and comparing these two results gives the final expression for k_{xp}:

$$\alpha k_{xp} = D_{eff} \ln\left(\frac{\phi_C}{a_C}\right) \tag{16}$$

where

$$D_{eff} = \frac{4D_{O_2}fD_{CO}n_{CO}}{2D_{O_2} + fD_{CO}n_{CO}} \tag{17}$$

Here, D_{eff} is the effective diffusion coefficient; it reduces to $2fD_{CO}n_{CO}$ if O_2 diffusion is much faster than the transport of CO, and conversely to $4D_{O_2}$ if oxygen diffusion is rate controlling. The parameter α depends on the composition of the substrate, SiC_xO_y. *Thus Eq. (16) embodies the key variables in the problem—the composition of the substrate, the activity of carbon in the atmosphere, the activity of carbon in the substrate, the diffusivity of oxygen and the permeability of carbon monoxide—and relates them to the experimental parabolic rate constant.* Before proceeding to apply Eq. (16) to the experiments, we note that by Henry's law the activity of carbon in the substrate, φ_C, may be written as the product of the activity coefficient, γ_C, and the mole fraction of carbon in the substrate, which we call χ_C in the following manner:

$$\phi_C = \gamma_C \chi_C \tag{18}$$

IV. Experimental Procedure

(1) Sample Preparation

Samples with four different levels of carbon composition were prepared. They were made by two methods. The two with the lower carbon content, TD2 and MTES, were obtained via the sol–gel route. The other two were made by catalytic cross-linking of polysiloxanes, PHMS-DVB20 and PHMS-DVB60. The final compositions of these ceramics are shown in Fig. 1.

The sample TD2 was produced by cohydrolysis of triethoxysilane, $HSi(OEt)_3$, and methyldiethoxysilane, $HMeSi(OEt)_2$, in a 2:1 ratio. The MTES sample was produced from methyltriethoxysilane, $Me\text{-}Si(Oet)_3$. All chemicals were obtained from ABCR (Karlsruhe, Germany). Gel rods approximately 30 mm × 8 mm where produced. The rods were cut into thin discs (ca 1-mm thick), that were pyrolyzed (see below), giving dense and crack-free SiCO discs. Full details of the sol–gel process are given in Soraru *et al.*[2]

The samples PHMS-DVB20 and PHMS-DVB60 were prepared by mixing a linear polymer polymethylhydrosiloxane (PHMS, MW = 2000, purchased from UCT, Briston, PA) with divinylbenzene (DVB purchased from Aldrich-Sigma, Milwaukee, WI) in ratios of DVB/PHMS = 20 and 60 wt%. An extremely efficient hydrosilylation catalyst, platinum divinyltetramethyldisiloxane (5 ppm relative to the amount of PHMS, purchased from Gelest, Morrisville, PA), was added to the mixed reagents without an additional solvent. This low-viscosity mixture was then poured into flat Petri dishes to form a layer 1–3-mm thick. The dishes were covered and let stand at room temperature overnight. Monosubstitution and disubstitution of the divinylbenzene occurs via hydrosilylation reaction,

Table I. Chemical Compositions and Parabolic Rate Constants

Sample	Composition	χ_C	k_{xp} (nm^2/s)	α	αk_{xp} (nm^2/s)
TD2	$SiC_{0.31}O_{1.39}$	0.12	1211 ± 10	0.46	557 ± 10
MTES	$SiC_{0.68}O_{1.51}$	0.21	1195 ± 55	0.58	693 ± 55
PHMS-DVB20	$SiC_{1.72}O_{1.07}$	0.45	736 ± 45	1.32	971 ± 45
PHMS-DVB60	$SiC_{2.71}O_{1.13}$	0.56	786 ± 60	1.92	1509 ± 60

converting the low-viscosity liquid into a hard, brittle rubber. Fragments of approximately 1 cm × 2 cm were obtained for pyrolysis.

All four kinds of specimens were pyrolyzed in a graphite crucible in a graphite furnace (Astro, Technology Instrument, Santa Barbara, CA) at a heating rate of 5°C/min to 1200°C, and then held at this temperature for 1 h. The pyrolysis was carried out in flowing Ar at 100 cc/min.

The gel-derived specimens were analyzed for Si, C, and H by the service d'Analyse Elementaire du CNRS (Vernaison, France). The O content was calculated by difference between the total weight and the sum of the weight of these three constituents. The PHMS-derived materials were analyzed for Si, C, and H contents by Galbraith Laboratory, USA (Albany, OR) and for O by Wei Chan Laboratory (Knoxville, TN). XRD spectra were collected using a Rigaku diffractometer D-max B (Rigaku, The Woodlands, TX) operating at 40 kV and 30 mA. The specific surface area (SSA) measurements were performed with a Micromeritics ASAP 2010. The XRD spectra (not shown here) suggest that the samples were predominantly amorphous, with the gel-derived materials containing very few crystallites of nanoscale SiC.[13] The BET analysis for all the samples gave a specific surface area value that was lower than 1 m^2/g, suggesting the formation of fully dense SiCO materials without residual porosity. The compositions of the samples are given in Table I.

(2) Oxidation Behavior

The oxidation experiments were carried out at 1350°C in ambient air atmosphere. The oven, lined with alumina, was preheated to this temperature. The samples, placed in an alumina crucible, were inserted into the furnace. After a selected length of time, ranging from less than an hour up to more than 100 h, the samples were extracted, fractured, and the thickness of the oxidation overgrowth silica layer measured by SEM. A typical image of a fracture surface is shown in Fig. 3. A dense, bubble-free oxide layer was observed for the three samples with the lower carbon concentrations. However, the sample with the highest carbon, when oxidized for more than 80 h, showed the presence of intermittently spaced stringers of bubbles, aligned parallel to the interface as in Fig. 4. The same samples oxidized for shorter periods (<80 h) did not exhibit bubble formation.

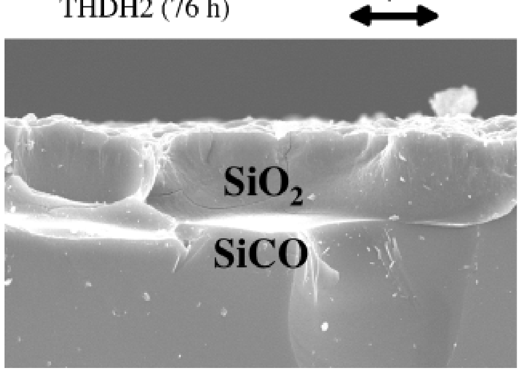

Fig. 3. Typical micrograph of the silica overlayer in the three samples with the lower carbon content.

The thickness of the silica overgrowth was measured from the SEM micrographs. At least 5 measurements were taken in different parts of the sample for each data point. The results are plotted as a function of the square root of time in Fig. 5. The slopes of linear fits to the data are the experimental values of k_{xp}. These values along with the error range in their estimate are listed in Table I. The values for α, Eq. (15), are also given.

V. Discussion of Results

(1) Estimating the Activity of Carbon

We apply Eqs. (16) and (18) to the data to obtain an understanding of the activity of carbon in the samples. The procedure is as follows. Combining these two equations gives:

$$\alpha k_{xp} = D_{eff} \ln \chi_C + D_{eff} \ln(\gamma_C / a_C) \qquad (19)$$

Therefore, a plot of αk_{xp} versus $\ln \chi_C$ should yield a linear fit, provided that Henry's law is obeyed, that is, the activity coefficient γ_C is a constant. In that case, Eq. (19) may be expressed as

$$\alpha k_{xp} = D_{eff}(\ln \chi_C + \ln \gamma_C) + A \qquad (20)$$

where $A = D_{eff} \ln(1/a_C)$. Here A can rightly be assumed as a constant for experiments carried out at the same temperature, so that D_{eff} remains constant. The atmospheric activity of carbon may also reasonably be assumed to be constant (a reviewer has suggested that the CO diffusion to the surface of the specimen from the interior would create a high carbon activity at the gas–solid interface—this is highly unlikely since the diffusivity of CO in the silica overgrowth is likely to be far, far slower than the diffusion of CO from the specimen surface into the ambient atmosphere, because the first is controlled by solid state diffusion and the second by the viscosity of gas at atmospheric pressure).

The application of Eq. (20) to experiments is shown in Fig. 6 where αk_{xp} is plotted versus $\ln \chi_C$. The first three points fit a reasonable straight line. The slope of this line yields a value for the effective diffusion coefficient, $D_{eff} = 3.3 \times 10^{-16}$ m^2/s.

The data in Eq. (20) can also be used to estimate a value for the activity coefficient, γ_C, in the following way. The deviation of the point for the highest carbon concentration suggests that a new phase of carbon has formed. If we assume this carbon to be elemental graphite,[14] with $\varphi_C = 1$, then we may estimate the value of γ_C for the SiCO phase by a lateral shift of the curve to

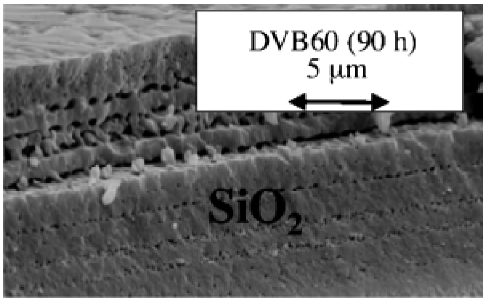

Fig. 4. Strings of bubbles, layered parallel to the interface in the sample with the highest carbon content.

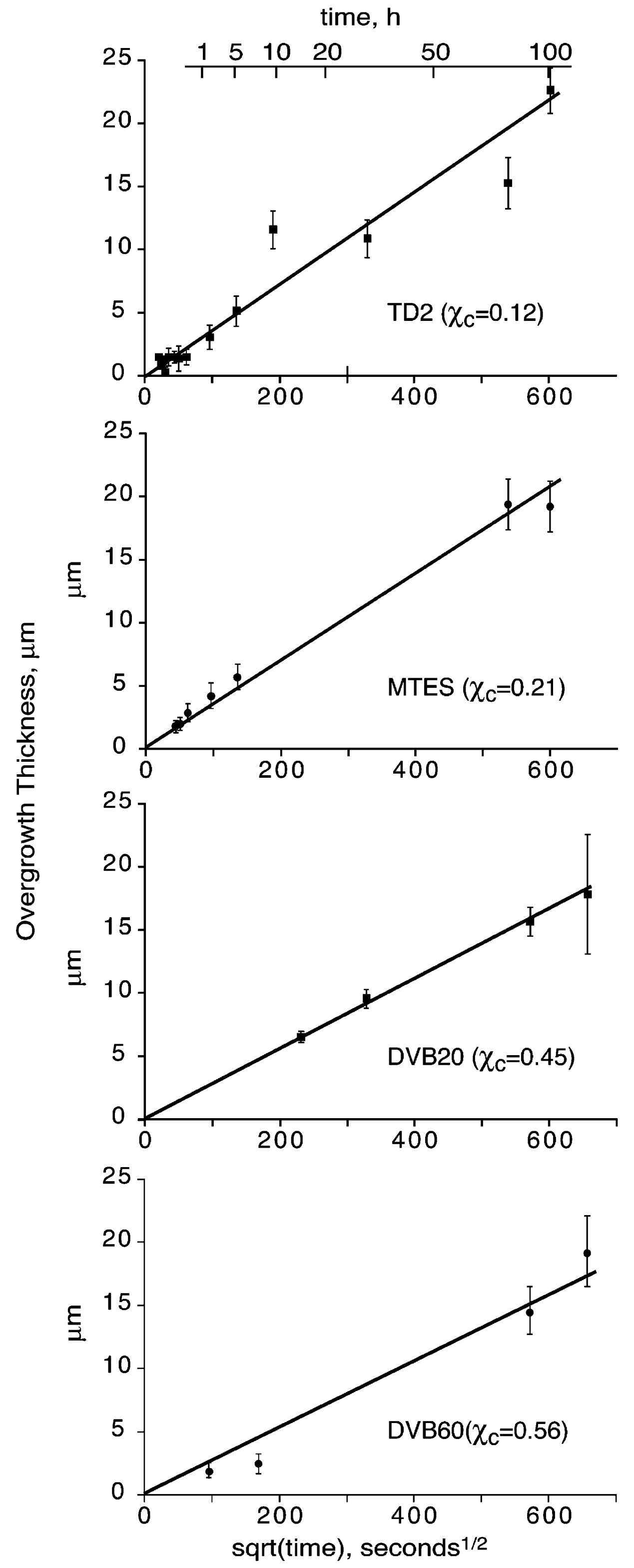

Fig. 5. Plots for the determination of the phenomenological parabolic rate constant, k_{xp}, for the four specimens.

the right until the activity of carbon in the highest carbon specimen, DVB60, is equal to one. This exercise yields a value for $\gamma_C = 2.1$, quite a reasonable number.

(2) Incipient Bubble Formation in the High Carbon Specimen (DVB60) at >80 h

The specimens with the highest carbon content apparently showed the presence of strings of bubbles, with the stringers being spaced intermittently normal to the surface, as shown in Fig. 6. Bubbles are sometimes seen in the oxidation of SiC[15] and at the asperities on the irregular surface of SiBCN.[16] The purpose here is to attempt to understand this behavior quantitatively. The approach is to investigate the possible values for the vapor pressure of CO at the interface, given by π_{CO} in Eq. (12), and invoke the condition that bubble formation becomes feasible if this pressure rises to one atmosphere.

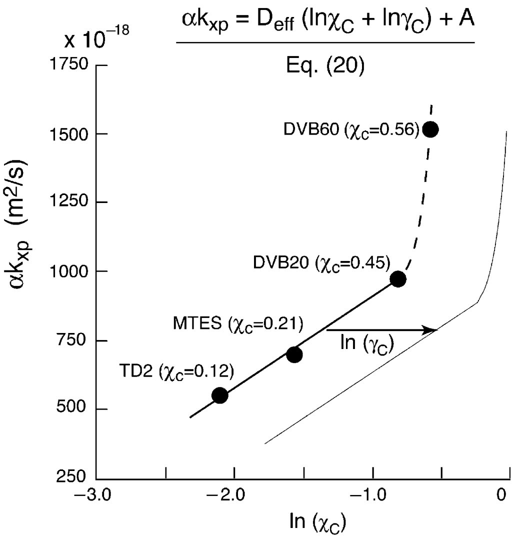

Fig. 6. A plot of the activity of carbon $\varphi_C = \chi_C\gamma_C$.

The equations for estimating π_{CO} are summarized in the Appendix. The analysis leads to three cases: (a) CO diffuses much faster than O_2, $\lambda \gg 1$, (b) the diffusivities are nearly the same, $\lambda = 1$, and (c) O_2 diffuses more quickly than CO, $\lambda \ll 1$.

Case (a) is ruled out because it requires the partial pressure of CO at the interface to be the same as in the atmosphere, which is clearly much less than unity. The third case is also not likely to apply, because it predicts pressures of the order of 10^8, which is untenable. In contrast, case (b), where the diffusivities of O_2 and CO are assumed to be nearly equal, gives a value of $p_{CO_2} = 240$ ppm, when $\pi_{CO} = 1$ and $\varphi_C = 1$. This value for atmospheric carbon dioxide is still a little high, but remember that it has been calculated by assuming the diffusion rates for CO and O_2 to be equal. A slight difference in the diffusivities would give a good agreement with experiment. Interestingly, Luthra[6] has speculated that the diffusivities of CO and O_2 in silica may be similar, since the molecular size of CO, 0.258 nm, is comparable to that of O_2 at 0.273 nm.

VI. Synopsis

This work set out to seek a quantitative understanding of: (a) the relationship between the parabolic rate constant for oxidation and the diffusivities of oxygen and carbon monoxide in the silica overgrowth during passive oxidation of carbonaceous ceramics; (b) the significance of the carbon activity in the material, and in the environment, in this process; and (c) the order of magnitude of the pressure of CO generated by the oxidation reaction at the interface. The results we have obtained are for the polymer-derived ceramic of a general composition SiC_xO_y. The results, of course, may be applied to crystalline silicon carbide, and with minor modification of the analysis to silicon nitride as well.

In a well-posed oxidation problem, the environmental activities of O_2 and carbon (which are controlled by the CO/CO_2 ratio) would be known. The activity of carbon in the substrate will also be a known quantity, as would be the permeabilities of oxygen and CO through silica. Therefore, the analysis that relates the growth rate of the overlayer to these quantities requires the knowledge of two unknowns, the partial pressure of O_2, and

CO, at the interface. The problem was solved using two equations: the constraint on the magnitudes of the O_2 and CO fluxes imposed by the composition of the substrate, and the chemical equilibrium between the activities (that is, the partial pressures) of O_2 and CO at the interface. These results are given in Eqs. (11) and (12). The simplicity of these results is intuitively satisfying: the interfacial activities, π_{O_2} and π_{CO}, depend on the ratio of the permeabilities of these two species through silica, specified by λ, and upon the ratio of the activities of carbon in the environment and at the interface, a_C/φ_C. With this solution in hand, the answers to the three questions posed above are obtained by simple algebraic manipulation.

The rate constant for parabolic growth of silica is obtained from the flux of oxygen. It is given in its final form in Eq. (16). It depends on the composition of the substrate, the ratio of the carbon activities mentioned above, and on the effective diffusivity, D_{eff}, given by Eq. (17). The equation for D_{eff} is such that the slower of the diffusing species controls the rate of oxidation. This result highlights the significance of the activity of carbon in the environment in the oxidation of carbides. The final result, the pressure of CO generated at the interface, is discussed in detail in the Appendix. Its magnitude depends critically on rate-controlling diffusion species in D_{eff}. Broadly speaking, these results suggest that if CO diffuses much more slowly than O_2, then very large pressures would develop at the interface that will surely cause bubble formation. The possibility of bubble formation is borderline if the two diffusivities are nearly equal, and bubble formation is unlikely if CO diffuses much faster than O_2. The present experiments suggest that the middle case, where the diffusivities are more or less equal, applies. Our observations are broadly in agreement with observations in the literature that suggest that bubbles are sometimes present, and often times not. Collectively these analytical results and experimental observations suggest that the oxygen and CO have comparable permeabilities in silica.

Finally, on the experimental side, we compare the present values for k_{xp} with those in the literature. Our experiments were done in ambient environments with values in the range of 700–1200 nm^2/s. In comparison, experiments with SiCNO ceramics (there does not appear to be any other data on SiCO) conducted by Chollon *et al.*[8] in *dry* air, gave values in the range 10–25 nm^2/s (at the same temperature). Recently, we have conducted oxidation studies on SiCO in dry oxygen environments as well, and find values for k_{xp} that are similar to those reported in Chollon *et al.*[8] We infer that humidity has a significant influence on the diffusion of oxygen and CO through silica.

Sometimes it is more useful to estimate the rate of consumption of the substrate upon oxidation than to measure the growth of the silica overlayer. This is easily done since, from Eq. (4), one mole of SiC_xO_y produces one mole of silica. One simply has to consider the ratio of the molecular weights (per silicon basis) and the densities to relate the growth rate of silica thickness to the recession rate of the substrate:

$$\frac{h_{silica}}{z_{SiCO}} = \frac{Mw_{silica}\,\rho_{SiCO}}{Mw_{SiCO}\,\rho_{silica}} \tag{21}$$

where h_{silica} (same as h) is the thickness of the silica scale, z_{SiCO} is the recession rate of the substrate, Mw_{silica} and Mw_{SiCO} are the molecular weights of silica and SiCO, and ρ_{silica} and ρ_{SiCO} are the densities of the two substances. The substitution of values in the right-hand side for the present materials shows that the recession rate is approximately the same as the growth rate of the silica overlayer.

Appendix. Estimating the Interfacial Pressure of CO

Equation (12) in the text, rewritten in the following form:

$$\pi_{CO} = p_{CO}\left(\frac{\phi_C}{a_C}\right)^{1/(1+\lambda)} \tag{A-1}$$

gives the pressure, π_{CO}. To make an estimate, we express p_{CO} and a_C in terms of the partial pressure of CO_2 and O_2 in the atmosphere. First we substitute for p_{CO} in terms of a_C, using the left side of Eq. (10). It then remains to write a_C as a function of the partial pressure of CO_2, which is achieved by enforcing equilibrium for the following reaction:

$$C + O_2 = CO_2 \tag{A-2}$$

which gives

$$a_C = \frac{p_{CO_2}}{p_{O_2}}\exp\left(\frac{\Delta G_{CO_2}}{RT}\right) \tag{A-3}$$

where ΔG_{CO_2} is the free energy for the above reaction. Upon making these substitutions into Eq. (A-1), the following result is obtained:

$$\pi_{CO} = p_{O_2}^{1/2}\left(\frac{p_{CO_2}}{p_{O_2}}\right)^{\frac{\lambda}{1+\lambda}}\phi_C^{\frac{1}{1+\lambda}}e^{\frac{1}{RT}\left(\Delta G_{CO_2}\frac{\lambda}{1+\lambda}-\Delta G_{CO}\right)} \tag{A-4}$$

where λ is given by Eq. (8). The values for the free energies, taken from the JANAF tables, are as follows:

$$\begin{aligned}\Delta G_{CO} &= -114 - 0.086T \text{ kJ/mol and}\\ \Delta G_{CO_2} &= -396 \text{ kJ/mol}\end{aligned} \tag{A-5}$$

It is interesting to consider three limiting conditions of Eq. (A-4): $\lambda \gg 1$, when CO diffuses much faster than O_2; $\lambda = 1$, when the diffusivities are nearly the same; and $\lambda \ll 1$, when O_2 diffuses more quickly than CO.

The case $\lambda \gg 1$ immediately leads to the expected result that interfacial and atmospheric pressure of CO must be nearly equal. This case clearly cannot lead to bubble formation, since the atmospheric pressure of CO is much less than unity.

The second case, where $\lambda = 1$ (Eq. (A-4)) reduces to:

$$\pi_{CO} = p_{CO_2}^{1/2}\,\phi_C^{\frac{1}{2}}\,e^{\frac{1}{RT}\left(\frac{1}{2}\Delta G_{CO_2}-\Delta G_{CO}\right)} \tag{A-6}$$

Substituting for ΔG_{CO_2} and ΔG_{CO} above gives:

$$\pi_{CO} = p_{CO_2}^{1/2}\phi_C^{1/2}e^{\frac{86T-83,500}{8.31T}}, \text{ when } \lambda = 1 \tag{A-7}$$

At 1350°C (T = 1623 K), Eq. (A-7) gives:

$$\pi_{CO} = 64\,p_{CO_2}^{1/2}\phi_C^{1/2} \quad \text{at} \quad T = 1623 \text{ K}, \lambda = 1 \tag{A-8}$$

In the third case, ($\lambda \ll 1$), oxygen is assumed to diffuse much faster than CO. Setting $\lambda \ll 1$ in Eq. (A-4) we obtain:

$$\pi_{CO} = p_{O_2}^{1/2}\phi_C e^{\frac{-\Delta G_{CO}}{RT}} \tag{A-9}$$

To calculate π_{CO} at 1350°C, we substitute for ΔG_{CO} from Eq. (A-5):

$$\pi_{CO} = 1.5\times10^8 p_{O_2}^{1/2}\phi_C \quad \text{at} \quad T = 1623\,K,\ \lambda \ll 1 \tag{A-10}$$

The three cases are discussed in the main text.

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