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The Role of Condensed Silicon Monoxide in the Active-to-Passive Oxidation Transition of Silicon Carbide

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Abstract

The critical condition for protective layer formation on SiC in terms of $P(O_2)$ and temperature is determined by the partial pressure of the product gases ($SiO_{(g)}$, CO) from the reaction between the substrate (SiC) and oxidic layer and the diffusion properties of the product gases and oxygen in a boundary layer.

The role of condensed silicon monoxide ($SiO_{(l)}$) as a possible form of protective layer has been assessed and an estimate of ΔH_f and ΔS_f for condensed SiO at 1727°C has been derived.

Both the thermodynamics of the Si–C–O system and recent experimental data on the active-to-passive oxidation transition for silicon carbide suggest the reaction defining this transition in terms of $P(O_2)$ and temperature to change with carbon activity. At high carbon activities the incompatibility between SiC and SiO_2 marks the transition, while at lower carbon activities and high temperatures the incompatibility between SiC and $SiO_{(l)}$ determines the transition.

The formation of a duplex layer of $SiO_{(l)}$ and SiO_2 is likely at high temperatures. The chemical interaction within this duplex layer could cause bubble formation/spallation at 1700–1800°C, because the CO pressure developed at the interface exceeds ambient pressure.

Die kritischen $P(O_2)$- und Temperaturbedingungen für die Ausbildung einer oxidischer Schutzschicht auf SiC werden durch den Partialdruck der Gasspezies $SiO_{(g)}$ und CO und den Diffusionskoeffizienten für diese und O_2 bedingt. $SiO_{(g)}$ und CO sind die Produkte einer Reaktion zwischen Substrat (SiC) und oxidischer Schicht.

Die Rolle von kondensiertem Siliziummonoxid ($SiO_{(l)}$) als möglicher Form der oxidischen Schutzschicht wurde evaluiert und eine Abschätzung für ΔH_f und ΔS_f von $SiO_{(l)}$ bei 1727°C (2000 K) erzielt.

Sowohl die Thermodynamik des Si–C–O Systems als auch neuere experimentelle Daten zum Übergang von aktiver zu passiver Oxidation von Siliziumcarbid legen nahe, daß der durch $P(O_2)$ und Temperatur beschriebene Übergang sich mit der Kohlenstoffaktivität ändert. Bei hoher Kohlenstoffaktivität ist die Inkompatibilität von SiC und SiO_2 übergangsbestimmend, während bei niedrigerer Kohlenstoffaktivität und hohen Temperaturen die Inkompatibilität von SiC und kondensiertem $SiO_{(l)}$ die Übergangsbedingung beschreibt.

Die Ausbildung einer Duplexschicht aus SiO_2 und $SiO_{(l)}$ ist bei hohen Temperaturen möglich. Die chemische Interaktion innerhalb dieser Duplexschicht kann bei ca. 1700–1800°C zu Blasenbildung und Abplatzen führen, da der äußere Druck durch den hier entwickelten CO-Druck überschritten wird.

Les conditions critiques de pression $P(O_2)$ et de température pour la formation d'une couche de protection oxyde autour de SiC sont determinées par les pressions partielles de gaz de $SiO_{(g)}$ et CO et par les coefficients de diffusion de SiO, CO et O_2. $SiO_{(g)}$ et CO sont les produits d'une réaction entre le substrat (SiC) et la couche oxyde.

On a étudié le rôle de $SiO_{(l)}$ condensé en tant que forme possible de la couche d'oxyde protectrice et on a réalisé une évaluation de ΔH_f et ΔS_f pour SiO à 1727°C (2000 K). La thermodynamique du système Si–C–O ainsi que les récents résultats expérimentaux sur le passage d'une oxydation active à une oxydation

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passive de SiC suggèrent tous deux que la réaction définissant cette transition en termes de pression $P(O_2)$ et de température dépend de l'activité du carbone. Pour de hautes activités, l'incompatibilité entre SiC et SiO_2 détermine la transition, tandis que pour des activités plus faibles à haute température, c'est l'incompatibilité entre SiC et $SiO_{(l)}$ qui la détermine.

La formation d'une double couche $SiO_{(l)}$ et SiO_2 est probable à température élevée. La réaction chimique à l'intérieur de la double couche peut provoquer la formation de bulles et al spallation à 1700–1800°C, étant donné que la pression de CO à l'interface dépasse la pression ambiante.

1 Introduction

SiC is a ceramic material which has a high oxidation resistance[1–3] in atmospheres dominated by oxygen. Thus it is useful for applications such as heating elements to ≈ 1600°C.

The excellent oxidation resistance comes from the formation of a protective layer essentially consisting of $\mathrm{SiO_2}$. However, if the atmosphere is reducing this layer is no longer formed and the material is free to react with its environment. In this case SiC may react very rapidly with metals such as Fe and Ni to form silicides and liquids at temperatures even below 1000°C.[4] It may also react with other gas species in an 'active' oxidation mode, i.e. it is decomposed to gaseous species.

For the application of SiC at high temperatures it is thus crucial to be aware of the limits of the protective $\mathrm{SiO_2}$-film production on SiC ('passive oxidation'). The transition to the active oxidation mode is usually described in terms of a critical $P(\mathrm{O_2})$ at a given temperature. The theoretical derivation of this transition has been described by Wagner[5] and is briefly outlined below.

The experimental data of Gulbranson *et al.*[6] and Hinze & Graham[7] on the active-to-passive transition in the oxidation of silicon carbide have recently been supplemented by Vaughn and Maahs.[8] These new data confirmed that the theories of Singhal[9] and Schiroky[10] do not describe the transition temperature–$P(\mathrm{O_2})$ conditions adequately.

Condensed silicon monoxide may play a vital role in the active-to-passive transition. Although known for a few years,[11] thermodynamically described[12] and even commercially available as an amorphous substance[13] condensed silicon monoxide has so far not been considered in the studies on the active-to-passive oxidation transition.

2 The Wagner Theory

Most investigators on the problem of active and passive oxidation agree with a theory described first by Wagner,[5] who discussed the problem for the case of metallic silicon. The thermodynamic stability of $\mathrm{SiO_2}$ based on the reaction

$$\mathrm{Si}_{(s,l)} + \mathrm{O}_{2(g)} \rightleftharpoons \mathrm{SiO}_{2(s,l)} \tag{1}$$

extends to very low oxygen partial pressures. At $P(\mathrm{O_2})$ conditions much higher than those predicted via reaction (1), Si begins to oxidise actively, i.e. it is consumed according to

$$\mathrm{Si}_{(s,l)} + \tfrac{1}{2}\mathrm{O}_{2(g)} \rightleftharpoons \mathrm{SiO}_{(g)} \tag{2}$$

The solution of this problem is thought to be a transport problem (Fig. 1). A boundary layer exists in the atmosphere next to the material in question, because oxygen is used up very rapidly at the interface by reaction (2), producing a partial pressure P^*_{SiO} at the gas/material interface. The product gas ($\mathrm{SiO}_{(g)}$) has to diffuse outwards while $\mathrm{O_2}$ is diffusing towards the material surface. Accordingly a gradient of $P(\mathrm{O_2})$ and $P(\mathrm{SiO}_{(g)})$ is established, depending on the individual effective thickness of the boundary layer for each species ($\delta(\mathrm{O_2})$, $\delta(\mathrm{SiO}_{(g)})$) and their diffusion coefficients ($D_{\mathrm{O_2}}$, D_{SiO}). The P^*_{SiO} may hence be related to the $P_{\mathrm{O_2}}$ in the bulk gas by

$$P^*_{\mathrm{SiO}} = 2\,P_{\mathrm{O_2}}\frac{\delta_{\mathrm{SiO}}D_{\mathrm{O_2}}}{\delta_{\mathrm{O_2}}D_{\mathrm{SiO}}} \tag{3}$$

The critical pressure of $\mathrm{SiO}_{(g)}$ is given by the reaction

$$\tfrac{1}{2}\mathrm{Si}_{(s,l)} + \tfrac{1}{2}\mathrm{SiO}_{2(s,l)} \rightleftharpoons \mathrm{SiO}_{(g)} \tag{4}$$

because at equilibrium the $P(\mathrm{SiO}_{(g)})$ for this reaction defines the compatibility between the substrate and the oxide layer (one may view this also as the condensation of $\mathrm{SiO}_{(g)}$). This $\mathrm{SiO}_{(g)}$ pressure also determines via eqn (3) also the critical oxygen partial pressure $P(\mathrm{O_2})_{\mathrm{max}}$. Using the relation

$$\frac{\delta_{\mathrm{SiO}}}{\delta_{\mathrm{O_2}}} = \sqrt{\frac{D_{\mathrm{SiO}}}{D_{\mathrm{O_2}}}} \tag{5}$$

Wagner[5] derived the estimate of $P(\mathrm{O_2})_{\mathrm{max}}$:

$$P(\mathrm{O_2})_{\mathrm{max}} = \frac{1}{2}\sqrt{\frac{D_{\mathrm{SiO}}}{D_{\mathrm{O_2}}}}\,P(\mathrm{SiO}_{(g)})\mathrm{eq} \tag{6}$$

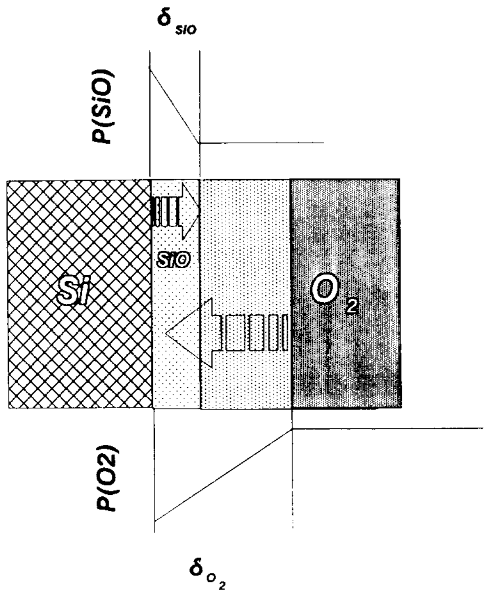
where $P(\mathrm{SiO}_{(g)})_{\mathrm{eq}}$ is the $P(\mathrm{SiO}_{(g)})$ calculated for reaction (4).

This compatibility between substrate and oxide layer may be called the 'primary' active/passive oxidation transition, because here the oxide cannot form. There are situations where the pressure of the

$Si + \frac{1}{2} O_2 \longrightarrow SiO(g)$

$Si + O_2 \longrightarrow SiO_2$

$Si + SiO_2 \longrightarrow 2\ SiO(g)$



$$P(SiO)^* = 2\,P(O_2)^{\circ}\ \frac{D_{O_2}\,\delta_{SiO}}{D_{SiO}\,\delta_{O_2}}$$

$$\text{Für Si:}\quad P(O_2)^{\circ} \approx 0.4 * P(SiO)_{eq}$$

Fig. 1. Schematic drawing illustrating the Wagner model:[5] In a boundary layer at the material/atmosphere interface gradients of $P(O_2)$ and $P(SiO_{(g)})$ are established through O_2 consumption and diffusion. The critical pressures are determined by the compatibility of substrate and oxide layer.

product gas exceeds the ambient pressure without exceeding the $P(O_2)_{max}$. In this case an oxide must form but is removed by spallation and bubble formation. Continuously repeating this process would be like an active oxidation, i.e. lead to a bare surface and overall weight losses. The critical condition for exceeding the ambient pressure could therefore be called a 'secondary' active/passive boundary.

3 Thermodynamics of the Si–C–O System

From a number of experimental studies[11] ΔH° and S° values have been estimated for amorphous and gaseous $SiO_{(g)}$ at 298 K ($\Delta H^{\circ}_{298} = -429\,697$ J mole^{-1}, $S_{298} = 46{\cdot}44$ J$*$mole$^{-1}*$K^{-1}, corresponding to $\Delta S^{\circ}_{f,298} = -74{\cdot}9$ J$*$mole$^{-1}*$K^{-1}). The uncertainty of the data is estimated by them to be 5–15%. Hard core information about condensed SiO includes the boiling point at 2160°C and its apparent instability at about 1100°C. Furthermore there are vapour pressure data, from which Nagamori *et al.*[12] extracted their estimate of $\Delta G^{\circ}_{f,298}$ for $SiO_{(l)}$ ($-452\,541 + 70{\cdot}79 * T$ (J mole^{-1})). This estimate conflicts with the decomposition at 1100°C, extending its stability to temperatures <1000°C.

The compilation of thermodynamic data[15] includes high temperature data for ΔH_f and S° of various phases in the Si–C–O system, but not condensed SiO. Most equilibria of interest in this study are at high temperatures. In order to get better estimates it is therefore preferable to work with high temperature data. Thus the thermodynamic data[15] have been used to calculate the values of ΔH_f and ΔS_f for the phases of interest at 1727°C (2000 K). Using these data (Table 1) an estimate of the thermochemical properties of $SiO_{(l)}$ at 2000 K is

Table 1. Thermochemical data used in this work

Phase	$\Delta H_{f,2000}$ $(J\,mol^{-1})$	$\Delta S_{f,2000}$ $(J\,K^{-1}\,mol^{-1})$
$C_{(s)}$	0	0
$CO_{(g)}$	−118 708	83·64
$O_{2(g)}$	0	0
$Si_{(s)}$	−49 363	−29·34
$Si_{(l)}$	0	0
$SiC_{(s)}$	−122 256	−36·81
$SiO_{(l)}$	−424 301	−60·09
$SiO_{(g)}$	−164 594	46·66
$SiO_{2(s)}$	−944 893	−196·91
$SiO_{2(l)}$	−935 279	−192·08

All data from JANAF tables except $SiO_{(l)}$, which was estimated in this study. Subscripts s, l and g refer to solid, liquid and gaseous states.

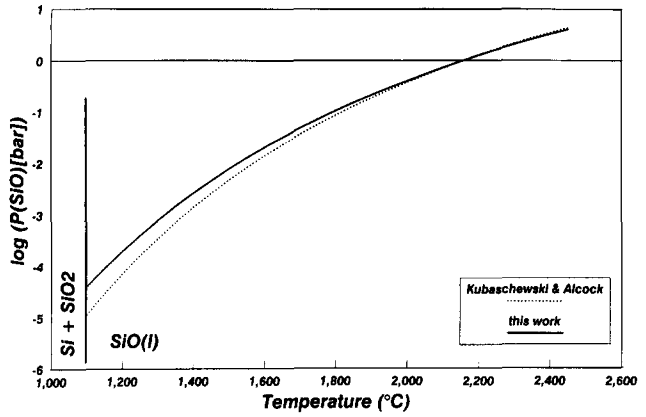


Fig. 2. Comparison of calculated vapour pressures using the appropriate equation from Ref. 11 and the estimate of thermodynamic properties of $SiO_{(l)}$ at 2000 K of this study (Table 1).

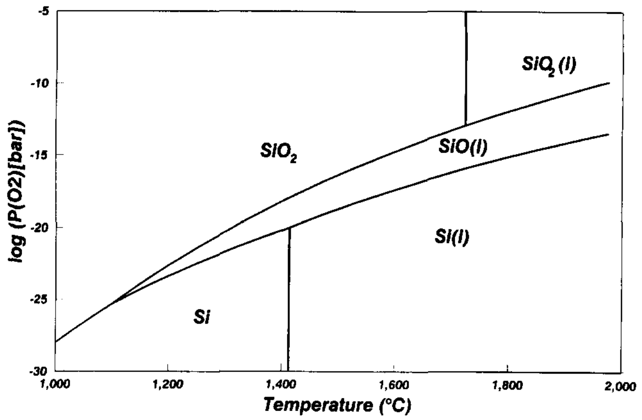


Fig. 3. Equilibrium phase relations in the Si–O system as calculated from data of Table 1.

obtained on the basis of boiling and decomposition points, i.e. the temperature for $P(SiO_{(g)}) = 1$ bar from the reaction

$$SiO_{(l)} \rightleftharpoons SiO_{(g)} \qquad (7)$$

and reaction (4). The estimate is included in Table 1.

Figure 2 shows the comparison of the calculated $SiO_{(g)}$ pressures using the newly estimated data and the three-term vapour-pressure equation of Ref. 11 which are particularly in good agreement for high temperatures.

The inclusion of the $SiO_{(l)}$ phase changes the phase diagram of the Si–O system. Figure 3 shows the stability region of $SiO_{(l)}$ in terms of temperature and oxygen partial pressure.

Accordingly at temperatures ≥1100°C the formulation of the Wagner model for the active/passive transition of Si should start to deviate from the estimate according to eqn (6), because the equilibrium pressure of $SiO_{(g)}$ at the gas/material interface is not determined by reaction (4) but by reactions (7) and (2).

Applying the Wagner model to SiC we may propose that active oxidation is characterised by the reaction

$$SiC_{(s)} + O_{2(g)} \rightleftharpoons SiO_{(g)} + CO_{(g)} \qquad (8)$$

and passive oxidation by

$$SiC_{(s)} + 1{\cdot}5\, O_{2(g)} \rightleftharpoons SiO_{2(s,l)} + CO_{(g)} \qquad (9)$$

In analogy with Si we have to find the reaction which defines the compatibility of substrate and oxide layer at equilibrium. For SiC the reactions

$$SiC_{(s)} + SiO_{2(s,l)} \rightleftharpoons 2\,SiO_{(g)} + C_{(s)} \qquad (10)$$

$$2\,SiC_{(s)} + SiO_{2(s,l)} \rightleftharpoons 3\,Si_{(l)} + 2\,CO_{(g)} \qquad (11)$$

$$SiC_{(s)} + 2SiO_{2(s,l)} \rightleftharpoons 3\,SiO_{(g)} + CO_{(g)} \qquad (12)$$

have been considered. Singhal[9] argued that thermodynamic equilibrium should favour reaction (12). Hinze & Graham[7] suggested CO to be the species of interest because reaction (11) is in better agreement with their data than (10) or (12).

In the Si–C–O system it is known that some oxidation/reduction reactions require intermediate rate-limiting steps such as SiC formation from SiO_2/C mixtures.[13] Thus it is not unreasonable to argue for a reaction producing metallic silicon to define the active/passive boundary, because once Si is formed it can be removed rapidly via reaction (2).

As pointed out by Nagamori *et al.*[12] it can be useful to include the concept of carbon activity (abbreviated αC in the following) to discuss SiC behaviour. At $\alpha C = 1$ free carbon is present or stable. An $\alpha C \leq 1$ can be visualised as carbon being present in some diluted form, e.g. as part of the grain boundary phase or dissolved within SiC. Figure 4 shows that αC may not drop below 10^{-2} in the presence of SiC at temperatures ≥ 1400°C.

Thus as long as SiC physically exists carbon activities are at the level of $\alpha C \approx 1$–0·01. Furthermore, sintered SiC usually contains free C, fixing αC at 1 as long as it is present. These facts limit the range of chemical conditions to be considered.

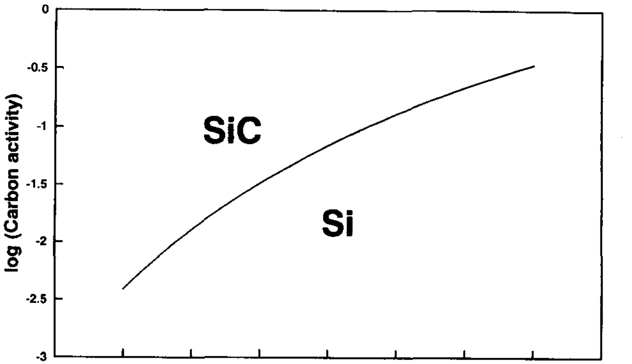


Fig. 4. Range of possible carbon activities in the presence of SiC and/or metallic silicon.

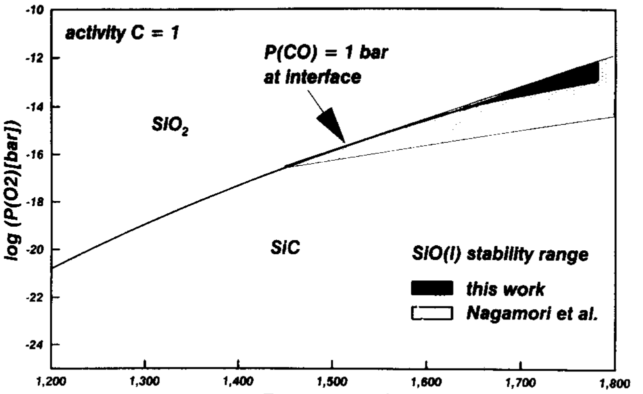


Fig. 5. Equilibrium phase relations in the S–C–O system for an activity of carbon = 1 (after Nagamori *et al.*[12] and this work).

In this study it is still preferred to plot in terms of the less abstract gas activities (which equal their pressure if treated as an ideal gas) but to define the carbon activity in the limits of the problem. The thermodynamic calculation fixes in this case the oxygen partial pressures to the C–CO equilibrium with the appropriate carbon activity (discussed in detail by Nagamori *et al.*[12]).

At a carbon activity of 1 Nagamori *et al.*[12] calculated that SiC and SiO_2 do coexist up to 1450°C and are separated by a stability region of $SiO_{(l)}$ at higher temperatures (Fig. 5). Lowering the activity of carbon to 10^{-1} expanded the stability region to cover a wide range of temperatures (Fig. 6). Using the estimate of the high temperature properties of $SiO_{(l)}$ derived in this study the stability region at $\alpha C = 1$ is shifted to much higher temperatures ($T \geq 1650$°C, Fig. 5) but indicates a stability region for $SiO_{(l)}$ down to ≈ 1350°C at $\alpha C = 0{\cdot}1$ (Fig. 6).

As indicated in Fig. 5 the CO pressure at the SiC–SiO_2 interface with $\alpha C = 1$ would exceed 1 bar at temperatures above 1520°C, i.e. any free carbon should be removed fast and αC could be lowered.

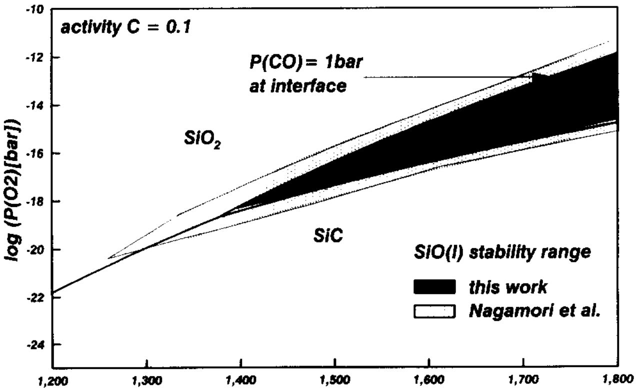


Fig. 6. Equilibrium phase relations in the Si–C–O system for an activity of carbon = 0·1 (after Nagamori *et al.*[12] and this work).

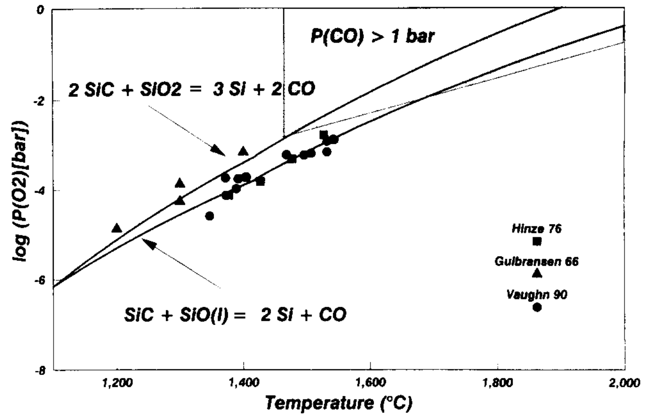


Fig. 7. Active-to-passive boundary of SiC in the Si–C–O system: experimental data and calculations from reactions as indicated. The shaded region is the 'secondary' boundary by spallation of bubbles (see text for discussion).

Inside the stability field of $SiO_{(l)}$ neither reactions (10), (11) nor (12) can be the rate limiting reactions, but

$$SiC_{(s)} + SiO_{(l)} \rightleftharpoons 2\,Si_{(l)} + CO_{(g)} \qquad (13)$$

because at a critical CO pressure this would be the first substance to condense. The removal of free Si would proceed via reaction (2), because a large mutual solubility of Si_l and $SiO_{(l)}$ is very unlikely.[12]

Calculating reaction (13) with the assumption that $\delta_{SiO}/\delta_{O_2} \approx D_{CO}/D_{O_2} \approx 1$ (1·02 according to Hinze & Graham[7]) the critical $P(O_2)$–T relations are plotted in Fig. 7 and compared to the experimental values. At temperatures below ≈ 1400°C the transition is close to that predicted from reaction (11), while at higher temperatures the results are close to values predicted from reaction (13).

This is in accordance with the thermodynamics: sintered SiC, containing free carbon, has a stable SiC–SiO_2–C–O boundary only at temperatures below 1520°C. Close to this temperature we have high equilibrium CO pressures, which may remove free carbon fast and hence lower the activity of carbon.

If free carbon cannot be removed fast enough the CO pressure will eventually exceed 1 bar creating a 'secondary' active-to-passive transition because large bubbles are inevitably formed and thus there will be an active-to-passive boundary by spallation. This boundary for the SiC–SiO_x interface is as low as 1520°C for high carbon activities, but will rise to approx. 2050°C for carbon activities appropriate for the coexistence of Si, SiC and $SiO_{(l)}$.

If however the oxidic layer on SiC can be described as consisting of an inner layer of $SiO_{(l)}$ and an outer layer of SiO_2 we will approach this large bubble formation region at temperatures of 1700–1800°C (depending on αC). Experimental evidence for the existence of this 'secondary' boundary has been presented by Schneider *et al.*[14] The 'secondary' transition may well be the ultimate boundary for the use of SiC at high temperatures in oxidising environments for long periods.

More work is needed to establish the thermochemical data of condensed SiO_2, in particular the possibility of a mutual solubility of SiO and SiO_2 should be investigated.[12] Qualitatively the role of $SiO_{(1)}$ in many processes involving silica-based materials is already becoming clear.

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