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# Effect of thermal treatment on the reactivity of SiC-based fibres

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The evolution of the chemical composition of the outer layer of SiC-based fibres was studied under different conditions of temperature and gas environment. After heating the fibres under vacuum or in argon at 1270, 1470, and 1570 K, their reactivity was determined with molecular oxygen at 1170 K and their surface composition was analysed by X-ray photoelectron spectroscopy. Treatment under a vacuum led to severe degradation of the fibres due to chemical reactions between SiC, $SiO_2$ and carbon. As a result, the silica layer initially present at the surface of the fibre disappeared and an oxygen-deficient silica compound was formed. On the contrary, the formation of silica at the fibre surface was observed during the treatment in argon and the chemical changes were more limited.

## 1. Introduction

Silicon carbide fibres are commonly used as fibrous reinforcements in ceramic matrix composites for applications at high temperature. The great advantage is that they form a protective silica layer in the presence of oxygen which limits their further oxidation. It is unlikely that their mechanical properties will dramatically decrease above 1470 K [1, 2]. In particular, a significant reduction of the tensile strength is observed above 1470 K following heat treatment in an inert atmosphere (vacuum or argon) which is related to chemical and microstructure changes [3]. The instability of these fibres must be considered with regard to the matrix/fibre coupling in ceramic composite fabrication and use. SiC-based fibre, obtained by pyrolysis of a polycarbosilane (PCS) precursor, is described as a multimaterial composed of silicon carbide (SiC), free carbon (C) and a non-stoichiometric silicon oxycarbide phase ($SiO_xC_y$) [4–6]. Thermodynamic calculations show that these fibres are inherently unstable when exposed to high temperature. Indeed, Johnson *et al.* [7] observed, using Knudsen cell mass spectrometry, that SiO and CO are produced when the fibres are exposed to temperatures higher than 1270 K under vacuum. Further works [8, 9] indicated that the released gases are, in part, attributed to the destruction of the $SiO_xC_y$ integranular phase and to the gasification of a fraction of the free carbon surrounding SiC crystallites. An endogeneous oxidation mechanism for the degradation of the fibre is then proposed following the overall equation

$$0.7SiO_{1.15}C_{0.85} + 0.42\,C \rightarrow 0.24\,SiO + 0.56\,CO + 0.46\,SiC \qquad (1)$$

It must be noted that this equation is established considering the global composition by weight of the fibre equal to 55% β-SiC crystals, 40% $SiO_{1.15}C_{0.85}$ and 5% free carbon. An important grain growth of SiC is also observed by transmission electron microscopy [9, 10] with a significant skin–core effect, the SiC crystallites being less developed in the inner part of the fibre. However, a recent study by multiple Knudsen cell mass spectrometry [11] completed by thermochemical calculations in the Si–C–O–H system [12] shows that $SiO_xC_y$ can be considered as a mixture of SiC, $SiO_2$ and C. Indeed, the SiC-based fibre exhibits a thermochemical behaviour similar to that of a (SiC + $SiO_2$ + C) mixed powder. Vahlas *et al.* [12] suggest a degradation mechanism according to the following scheme

$$3C_{(s)} + SiO_{2(s)} \rightarrow SiC_{(s)} + 2CO_{(g)} \qquad (2)$$

$$SiC_{(s)} + 2SiO_{2(s)} \rightarrow 3SiO_{(g)} + CO_{(g)} \qquad (3)$$

Reaction 2 is considered to be predominant in the temperature range where carbon, $SiO_2$ and SiC coexist, because Reaction 3 takes place after consumption of the free carbon. Moreover, the authors note that the weight loss is more important than thermodynamic calculations would indicate, and that it occurs at a much lower temperature than predicted. This difference may be attributed to the fact that the external part of the fibre is exposed to more severe degradation conditions. But no further investigations were made on the surface chemistry of the fibres. The objective of this work was to study the evolution of the chemical composition of the outer layer of SiC-based fibres after treatment at different temperatures above 1270 K and in various gaseous environments. In a previous study, it was shown that SiC and carbon phases in a SiC/C/SiC composite could be differentiated by their reactivity with molecular oxygen [13]. Therefore, after heat treatment under different conditions, the reactivity of the fibre with oxygen at 1170 K was determined and the composition of the outer layer was analysed using X-ray photoelectron spectroscopy (XPS).

## 2. Experimental procedure

### 2.1. Material

Commercial silicon carbide-based fibres (Nicalon NML 202) derived from polycarbosilane polymer precursor are used for this study. The manufacturing process of these fibres is abundantly described in the literature [14,15]. The as-received fibres, woven in two-dimensional layers, are covered with a polyvinylacetate sizing which is removed by heat treatment at 700 °C for 6 h in an argon flow. The elemental atomic composition of the fibres is 37% Si, 47% C and 16% O which would correspond to the following bulk molar composition per gram of fibre: 0.16 mmol SiC, 0.94 mmol C, 0.42 mmol $SiO_2$. Part of the silica consists in an external layer (mean thickness equal to 10 nm) which is formed during the industrial preparation of the fibre. This layer corresponds only to 12% of the molar fraction of $SiO_2$. The density, as indicated by the manufacturer, is equal to 2.55. The specific surface area, $S_{sp}$, of the fibre as measured by Krypton adsorption at 77 K, is equal to $0.11\ m^2\,g^{-1}$.

### 2.2. Heat treatment

The fibres were heated under vacuum or in argon at 1270, 1470 and 1570 K. The fibres, placed in an alumina crucible, were introduced into an alumina tube which was heated at $300\ K\,h^{-1}$ and held for 2 h at the chosen temperature. For treatment under vacuum, a residual pressure of $10^{-3}$ Pa was established in the tube. The gas evolved during thermal treatment was continually evacuated with a turbomolecular pump. For this run, the weight of the sample was 0.01 g. A quantitative analysis of the gaseous phase during treatment under vacuum was done by mass spectrometry as indicated elsewhere [16]. The second type of treatment was conducted under flowing argon ($60\ l\,h^{-1}$). The impurities content of argon was lower than 60 p.p.m. and consisted mainly in $O_2$ and $H_2O$. The runs were carried out with sample of 1 g sample by weight.

### 2.3. Reactivity measurement of the fibre

Following heat treatment under different conditions, the reactivity of the fibres was measured with oxygen. Experiments were carried out in a volumetric apparatus at 1170 K under 1 kPa oxygen. The sample was heated under a vacuum up to 1170 K in a fused silica glass system. Afterwards, a known amount of pure oxygen (purity better than 99.995% by volume) was introduced into the tube. The oxygen consumption and the formation of gaseous species (CO, $CO_2$ and $H_2O$) were quantitatively followed with a mass spectrometer (Balzers QMGHZ). The total pressure of the system was measured with a linear pressure gauge (Datametrics Barocel, pressure range (0–1.3 kPa)). The number of moles per gram of each species present in the gas phase at time $t$ can be calculated from the partial pressure of the gas given by mass spectrometry and the value of the total pressure. This experimental procedure is described in detail in a previous paper [13]. Relative experimental uncertainties lie within 10%.

### 2.4. XPS analysis

The fibre surface was characterized by X-ray photoelectron (XPS) measurements after each thermal treatment. The XPS spectra were recorded on a Leybold ($LHS\text{-}EA_{11}$) spectrometer, operating with $MgK_{a1,\,a2}$ radiation, an accelerating tension of 10 kV, an emission current of 30 mA, under ultra-high vacuum conditions ($3\times10^{-8}$–$2\times10^{-7}$ Pa). The fibre sample was deposited on an inox support. It was verified that the intensity of the peaks corresponding to the support was negligible compared to the peaks of the sample.

## 3. Results

### 3.1. Heat treatment

The weight losses of the fibres for different temperatures of treatment and environment are listed in Table I. The values indicated are the average of three runs. It appears that thermal treatment under vacuum or in argon at 1270 and 1470 K leads to a weak weight variation of the fibres. Nevertheless, a weight loss of about 25% was measured for the fibre treated under vacuum at 1570 K for 2 h. Interestingly, this value is close to the maximum weight loss value found by Jaskowiak and DiCarlo [3] (26%–28%) and corresponds to a complete degradation of the fibre. On the contrary, the weight loss was much smaller in argon at the same temperature. The nature and the quantity of the gases which were released during treatment under vacuum up to 1570 K were analysed by mass spectrometry. It was observed that the gaseous phase is mainly composed of carbon monoxide, hydrogen and water. The desorption rate of the released gases (CO, $H_2$ and $H_2O$) as a function of temperature is shown in Fig. 1. The total amount of released gases ($H_2$, CO and $H_2O$) at the end of the run is indicated in Table II.

It can be seen in Fig. 1 that a substantial amount of hydrogen is released between 1173 and 1470 K but its contribution to fibre weight loss is not significant (0.7%). The release of hydrogen is attributed to the breakage of C–H bonds located at the periphery of the basic structural units (BSUs) [17]. The amount of CO increases suddenly at 1493 K indicating a strong chemical modification of the fibre and represents 63% of the fibre weight loss. It is known that SiO is also formed at this temperature, but it cannot be detected in our experimental conditions due to its disproportionation before reaching the mass spectrometer.

### 3.2. Reactivity with oxygen of thermally treated fibres

Whatever the type of thermal treatment, carbon dioxide is the main gaseous product formed during fibre oxidation. No carbon monoxide was detected in our experimental conditions. Considering the oxygen

TABLE I Fibre weight loss for different heat-treatment conditions.

| Temperature (K) | Weight loss (%)<br>Vacuum | Argon |
|---|---|---|
| 1270 | < 1 | < 1 |
| 1470 | 5 | < 1 |
| 1570 | 25 | 1 |

TABLE II Amounts of gases released during thermal treatment of the fibre under vacuum up to 1575 K.

| Total weight loss = 25% at 1570 K<br>Gas released | Amount (mol g$^{-1}$) |
|---|---|
| CO | $5.6 \times 10^{-3}$ |
| $H_2$ | $1.3 \times 10^{-4}$ |
| $H_2O$ | $9.2 \times 10^{-4}$ |

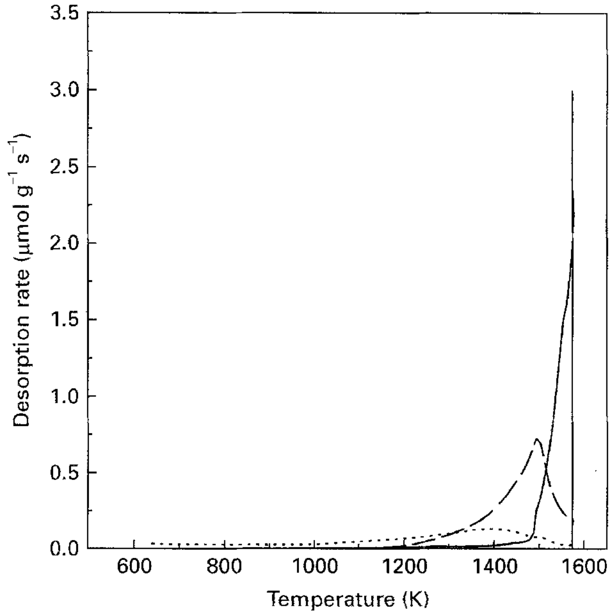

*Figure 1* Heat treatment of SiC-based fibres under vacuum: (—) CO, (– – –) $H_2$, (- - -) $H_2O$.

balance, it appears that all consumed oxygen was not converted into $CO_2$. Consequently, a fraction of the oxygen involved in the formation of silica, resulting from the oxidation of silicon carbide, according to

$$SiC(s) + 2O_2(g) \rightarrow SiO_2(s) + CO_2(g) \qquad (4)$$

Moreover, the free carbon present on the fibre can also react

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad (5)$$

The respective contribution of the oxidation of SiC (Reaction 4) and of the oxidation of the free carbon (Reaction 5) can be estimated by the ratio, $R$

$$R = \frac{N(C)}{N(O_2)_s} = \frac{N(CO_2)}{N(O_2)_s} \qquad (6)$$

where $N(C)$ is the number of moles of carbon gasified and $N(O_2)_s$ is the number of moles of oxygen needed for $SiO_2$ formation. For Reaction 4, $R$ is equal to 1. In contrast, $R \rightarrow \infty$ for Reaction 5, corresponding to the carbon gasification. More details of the calculation of the ratio $R$ are given elsewhere [13].

### 3.2.1. Reactivity of untreated fibres

The changes in $N(CO_2)$ and $N(O_2)_s$ are shown as a function of time in Fig. 2. During the first 40 min of reaction, carbon dioxide is formed in a significant amount, whereas fixation of oxygen is still negligible (Fig. 2a). Afterwards, $N(CO_2)$ and $N(O_2)_s$ increase steadily with oxidation time (Fig. 2b). The experimental plot $N(CO_2)$ versus $N(O_2)_s$ for the untreated fibre is shown in Fig. 3. Two distinct oxidation sequences are found. First, $CO_2$ is formed ($N(CO_2) = 15$ μmol g$^{-1}$) without any significant fixation of oxygen. Considering the specific surface area of the fibre equal to 0.11 m$^2$ g$^{-1}$, a carbon density equal to 2.0, the amount of gasified carbon corresponds to a layer with a thickness equal to 3 nm. This carbon is attributed partly to an incomplete

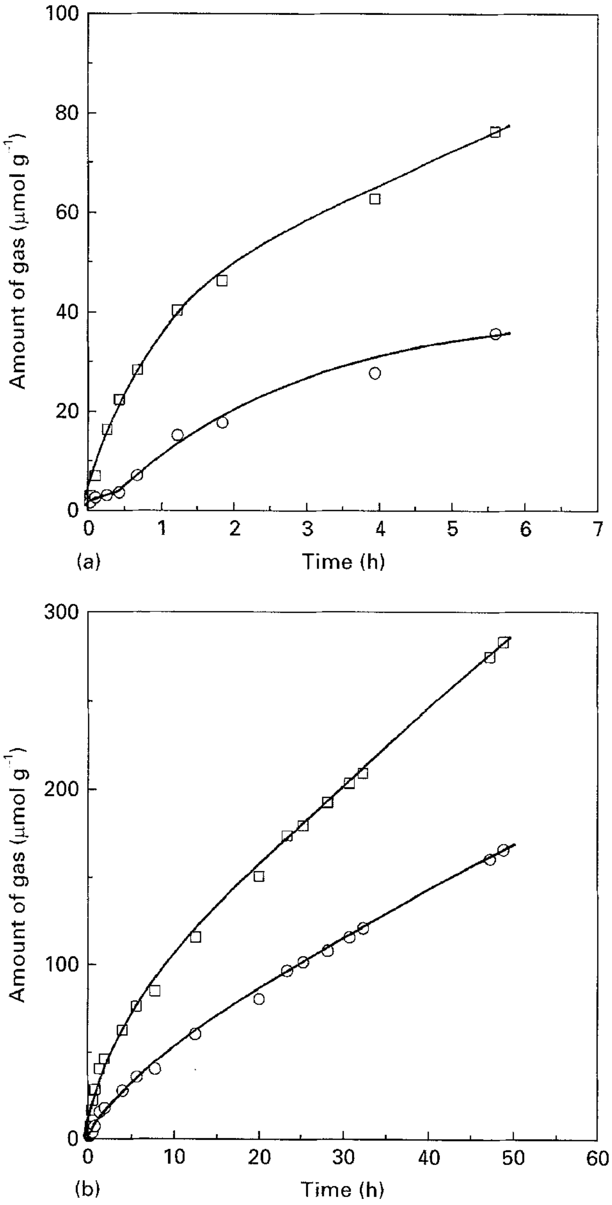

*Figure 2* Oxidation of untreated fibres at 1170 K as a function of time: (□) $CO_2$, (○) fixed oxygen.

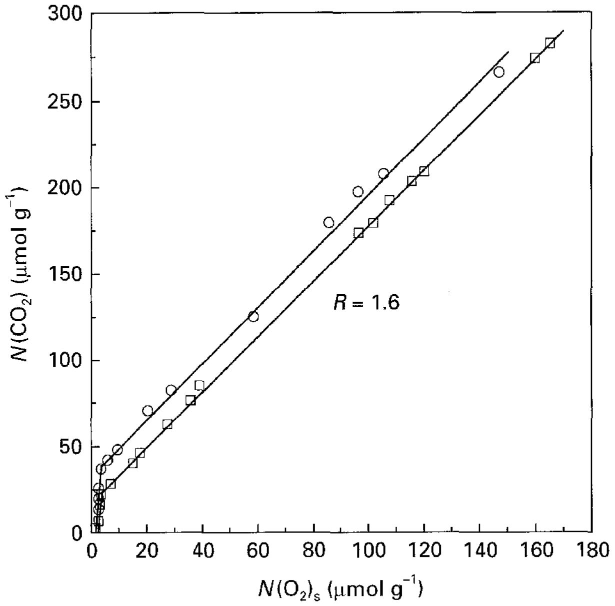

*Figure 3* Evolved $CO_2$ versus fixed $O_2$: (□) untreated fibres, (○) fibres treated at 1270 K under vacuum.

decomposition of the polyvinyl acetate during the desizing of the fibre, and also to a turbostratic layer initially present at the fibre surface [18]. After gasification of the free carbon present at the fibre surface, a linear relationship is obtained between the release of $CO_2$ and the fixation of $O_2$. The value of the slope is equal to 1.6 which indicates that SiC and free carbon are simultaneously oxidized ($R > 1$). A theoretical value of the ratio $R$ can be calculated from the bulk molar composition of the fibre by considering Reactions 4 and 5, and assuming similar oxidation rates. The theoretical value for $R$ is equal to 1.6 which is in agreement with the experimental one. Consequently, the reactivity of the untreated fibre with oxygen is characterized by a simultaneous oxidation of SiC and carbon which corresponds to the fibre stoichiometry after gasification of the free carbon layer on the surface.

### 3.2.2. Reactivity of fibres treated under vacuum

*3.2.2.1. Fibres treated at 1270 K.* The formation of $CO_2$ and the fixation of $O_2$ as a function of time for fibres heated in vacuum at 1270 K is similar to that obtained for the untreated fibres. The experimental plot $N(CO_2)$ versus $N(O_2)_s$ is compared to that obtained for the untreated fibres (Fig. 3). Comparison of both plots indicates that the treated fibres exhibit a similar behaviour in the presence of oxygen as the untreated fibres, i.e. gasification of the carbon layer and simultaneous oxidation of SiC and carbon. The amount of free carbon on the fibre is somewhat higher (45 μmol g$^{-1}$ instead 25 μmol g$^{-1}$ for untreated fibres) but the chemical composition of the fibre surface seems not to be really affected by thermal treatment at 1270 K under vacuum. This result is in agreement with the weak weight loss at this temperature (see Fig. 1 and Table I).

*3.2.2.2. Fibres treated at 1470 K.* The changes in $N(CO_2)$ and $N(O_2)_s$ are shown as a function of time in Fig. 4. It can be seen that the oxidation kinetic differs from the untreated fibres. During the first 20 min oxidation, the rates of formation of carbon dioxide and of fixation of oxygen are much higher than for the untreated fibres. The amounts of gasified carbon and of fixed oxygen are equal to 52 and 12 μmol g$^{-1}$, respectively (Fig. 4a). After 20 min oxidation the rates of formation of $CO_2$ and $O_2$ fixation become more or less similar (Fig. 4b). The shape of the plot $N(CO_2)$ versus $N(O_2)_s$ is quite different from that obtained for the untreated fibre (Fig. 5). In this case, three distinct sequences can be depicted. First, gasification of free carbon present at the fibre surface takes place because $N(CO_2) \gg N(O_2)$ after 20 min oxidation (sequence I). It appears also that the amount of carbon gasified at the end of the first sequence represents twice the amount present on untreated fibre. In the second sequence, the fixation of oxygen is more important than the release of carbon dioxide ($R < 0.75$). A value of $R$ lower than 1 suggests that a fraction of oxygen is chemisorbed without the formation of $CO_2$, i.e. it does not originate from the oxidation of SiC. Sequence III

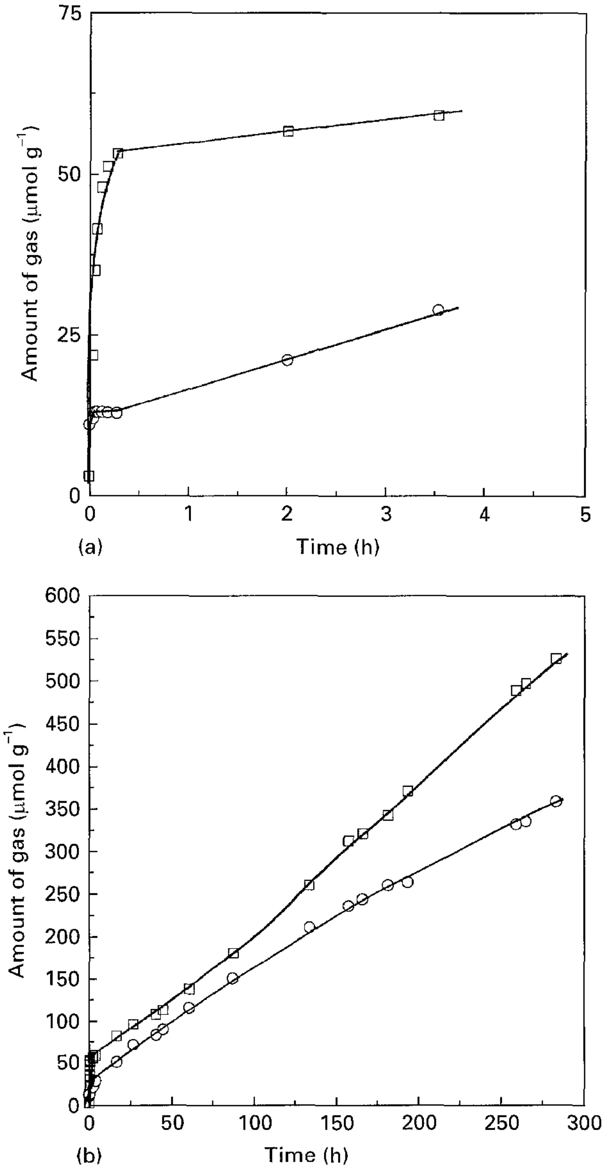

*Figure 4* Oxidation at 1170 K of fibres treated at 1470 K under vacuum as a function of time: (□) $CO_2$, (○) fixed oxygen.

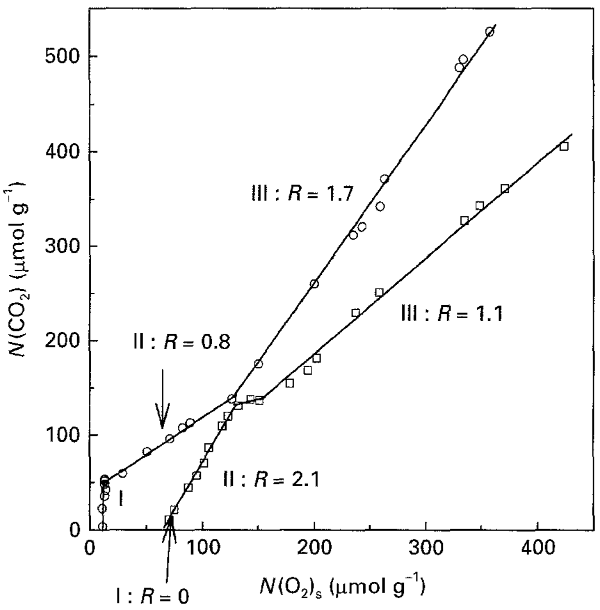

*Figure 5* Evolved $CO_2$ versus fixed $O_2$ for fibres treated under vacuum at (□) 1470 K, (○) 1570 K.

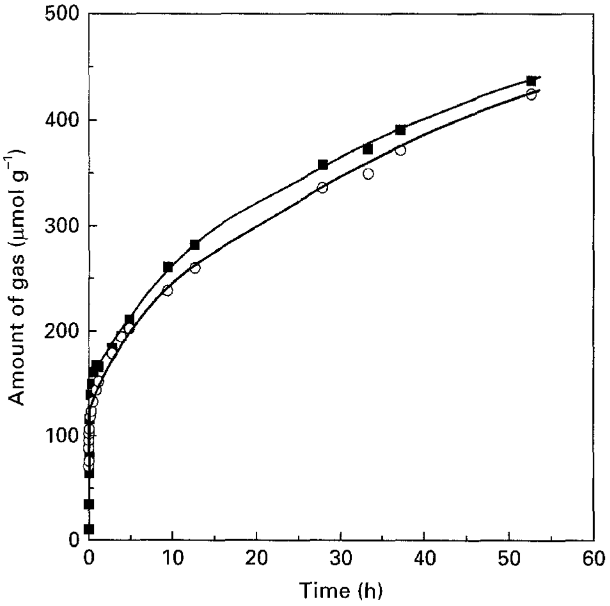

*Figure 6* Oxidation at 1170 K of fibres treated at 1570 K under vacuum as a function of time: (□) $CO_2$, (○) fixed oxygen.

begins when 140 $\mu mol\,g^{-1}$ $O_2$ have been fixed on the fibre. This sequence corresponds to an oxidation mechanism similar to that observed for untreated fibre, because the ratio of gasified carbon to chemisorbed oxygen is also equal to 1.6. Hence, it appears that chemical changes have occurred at the fibre surface during thermal treatment.

*3.2.2.3. Fibres treated at 1570 K.* The rate formation of $N(CO_2)$ versus $N(O_2)_s$ is represented in Fig. 6. After heat treatment at 1570 K, the reactivity of the fibre is increased again, because both $CO_2$ formation and oxygen fixation take place to a significant extent during the first hour of oxidation. The plot $N(CO_2)$ versus $N(O_2)_s$ (Fig. 5) indicates that an important amount of oxygen (70 $\mu mol\,g^{-1}$) is fixed during the first sequence. Preferential fixation of oxygen has already been noticed with fibres heated at 1470 K (sequence II, $R = 0.75$) but to a lesser extent than for the present case ($R \cong 0$). Afterwards, a transient step is observed at 1570 K with a slope $R$ equal to 2.1, suggesting that gasification of free carbon and oxidation of silicon carbide are taking place. In this sequence, the amount of gasified free carbon is equal to 50 $\mu mol\,g^{-1}$. It is interesting to note that a similar value was found for fibres heat treated at 1270 and 1470 K. After 1 h oxidation, a third sequence is found with a value $R = 1.1$. This value of $R$ suggests that mainly silicon carbide is oxidized and that free carbon is no longer present. The modification of chemical reactivity of the fibre is also accompanied by a change in the specific surface area of the fibre which significantly increases after treatment at 1575 K ($S_{sp} = 3.3\ m^2\,g^{-1}$).

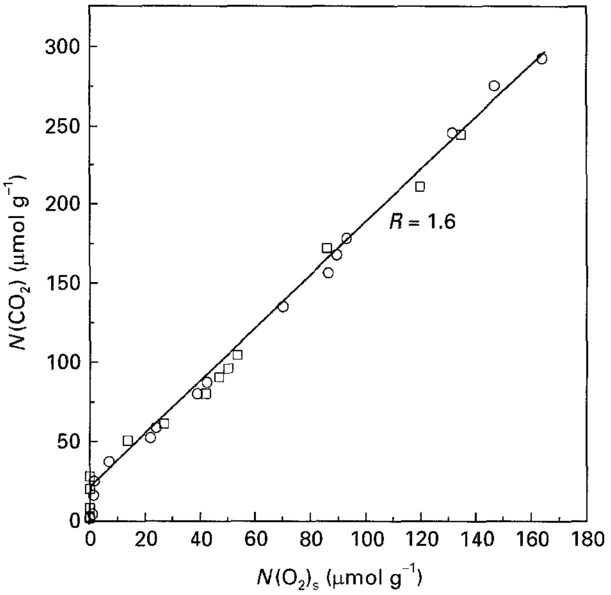

*Figure 7* Evolved $CO_2$ versus fixed $O_2$ for fibres treated in argon at (□) 1470 K, (○) 1570 K.

### 3.2.3. Fibres treated in argon

For fibres treated in argon, the oxidation kinetics are similar to those obtained for the untreated ones, as shown by the experimental plots $N(C)$ versus $N(O_2)_s$ (Fig. 7). A free carbon layer still seems to be present after the treatment. The value of the specific surface area after heating the fibre in argon is similar to that obtained for untreated fibre ($S_{sp} = 0.11\ m^2\,g^{-1}$). Hence, thermal treatment in argon does not significantly change the reactivity of the fibres with molecular oxygen.

## 3.3. XPS analysis

### 3.3.1. SiC-based fibres treated under vacuum

The C 1s and Si 2p core-level spectra of the untreated and the fibres treated at 1270, 1470 and 1570 K are compared in Figs 8 and 9, respectively. The different chemical components which result from the decomposition of the peaks are listed on each spectrum. For the C 1s core level spectra (Fig. 8), three major peaks

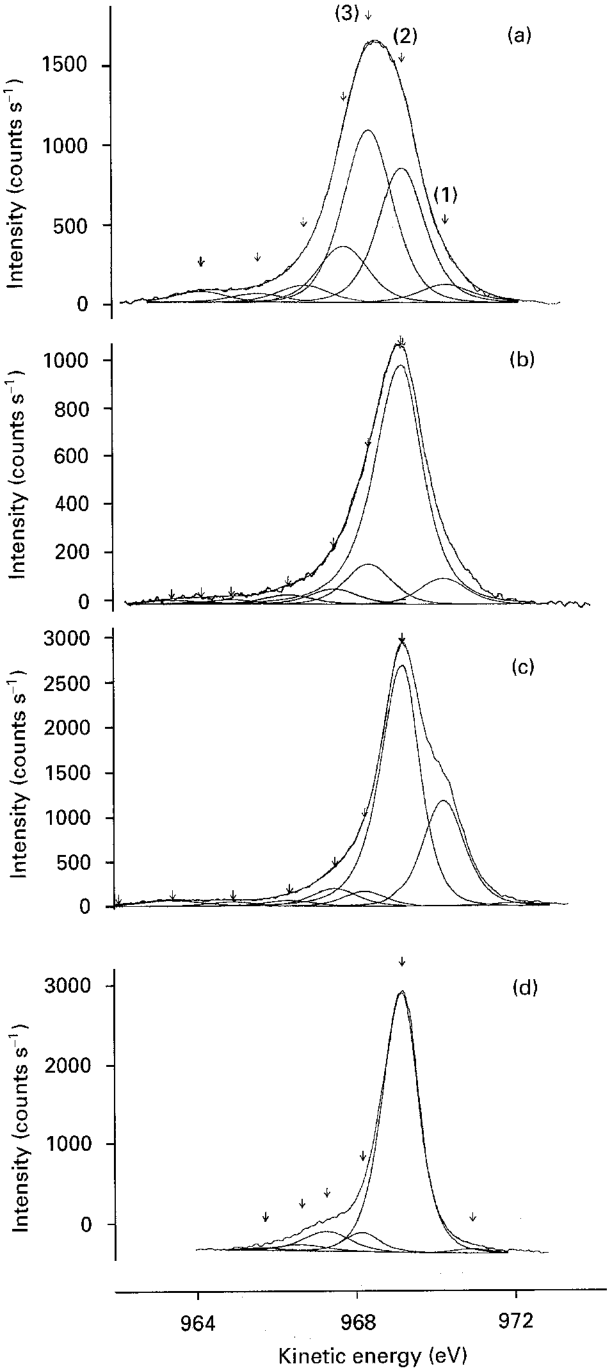

*Figure 8* C 1s core level spectra for (a) untreated fibres, (1) SiC, (2) C sp$^2$, (3) C–H, (b) fibres treated at 1270 K under vacuum, (c) fibres treated at 1470 K under vacuum, (d) fibres treated at 1570 K under vacuum.

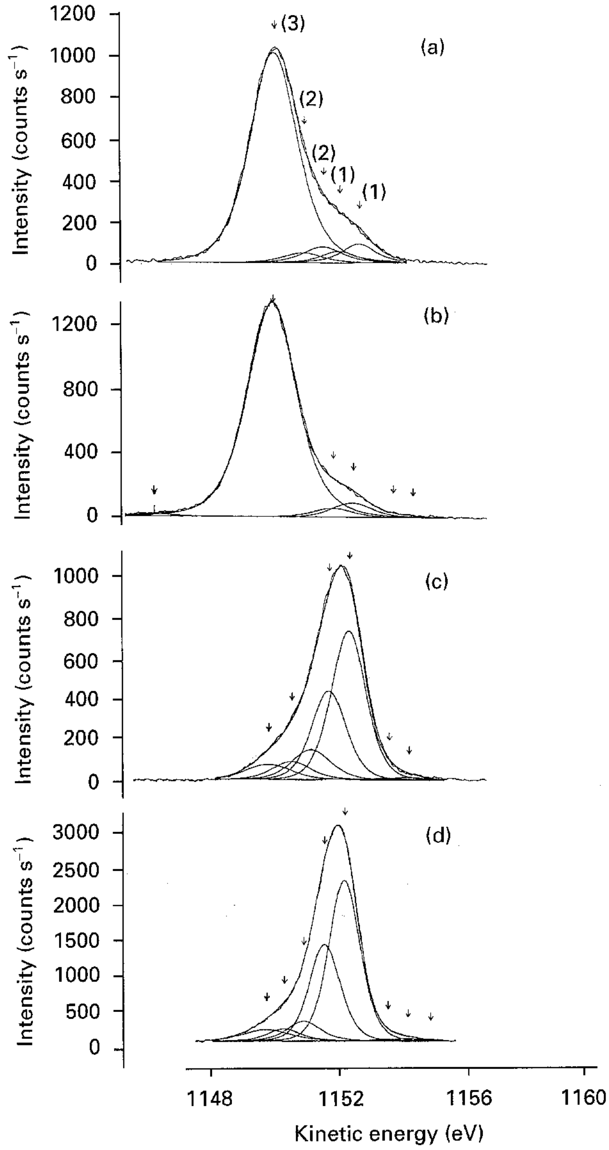

*Figure 9* Si 2p core level spectra for (a) untreated fibres, (1) SiC, (2) SiO$_x$C$_y$, (3) SiO$_2$, (b) fibres treated at 1270 K under vacuum, (c) fibres treated at 1470 K under vacuum, (d) fibres treated at 1570 K under vacuum.

appear corresponding to (1) silicon carbide, (2) turbostractic or graphitic carbon, (3) aliphatic carbon (including hydrocarbon). The contribution of peak 1 increases with thermal temperature and becomes largely predominant at 1570 K. Peak 2 increases after treatment at 1470 K but strongly decreases after heating the fibre at 1570 K. Finally, the intensity of peak 3 decreases rapidly with treatment temperature. The disappearance of peak 3 may be attributed to the fact that the aliphatic carbon undergoes a structure modification due to the heat treatment which corresponds to peak 2. In Fig. 9, for increasing binding energies, the decomposed peaks correspond to (1) SiC, (2) a non-stoichiometric silicon oxycarbide phase, SiO$_x$C$_y$, and (3) SiO$_2$. The contribution of silica strongly decreases after treatment at 1470 and 1570 K. On the contrary, the contribution of SiC increases with temperature, as already mentioned in the case of the C 1s core level spectra. Peak 2 remains constant as the treatment temperature increases.

The Si 2p spectrum of a fibre heat treated at 1570 K and exposed to oxygen at 1170 K for 5 min is shown in Fig. 10. This sample was examined after fixation of 70 μmol g$^{-1}$ oxygen without any release of CO$_2$ (see Fig. 5, sequence I). The XPS spectrum of the sample heated at 1570 K is also shown for comparison. It appears that after oxygen fixation, SiO$_2$ is found in the spectrum. This result indicates that a compound deficient in oxygen is formed after treatment at 1570 K under vacuum. It also suggests that the occurrence of an oxidation sequence with $R < 1$ after heat treatment at 1470 K is due to the presence of the same chemical structure. Hence, the compound with no well-defined XPS spectrum, but which leads to silica after oxygen chemisorption, will be called "oxygen-deficient silica" in the following. In some cases, a trace of Al$_2$O$_3$ could be detected. This contamination may result from the

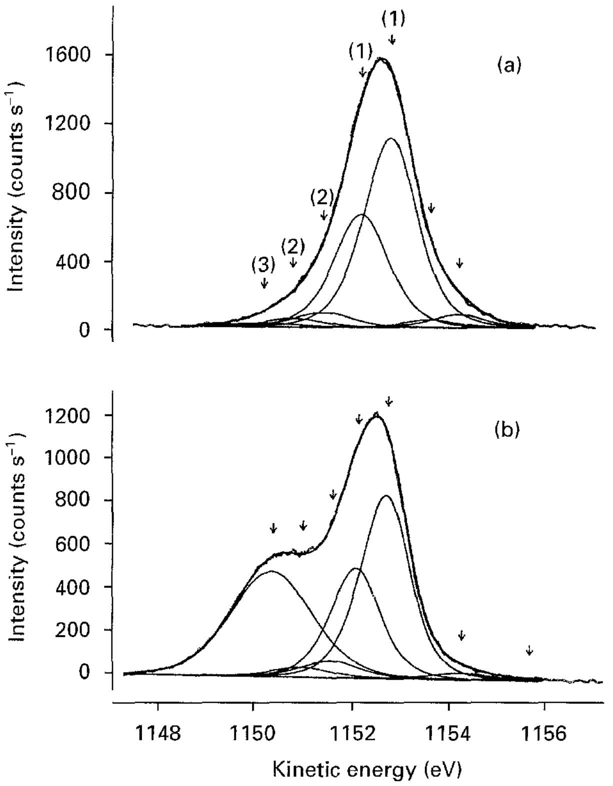

*Figure 10* Si 2p core level spectra of (a) fibres heated at 1570 K under vacuum, (1) SiC, (2) $SiO_xC_y$, (3) $SiO_2$, (b) fibres heated at 1570 K under vacuum and exposed to oxygen at 1170 K for 5 min.

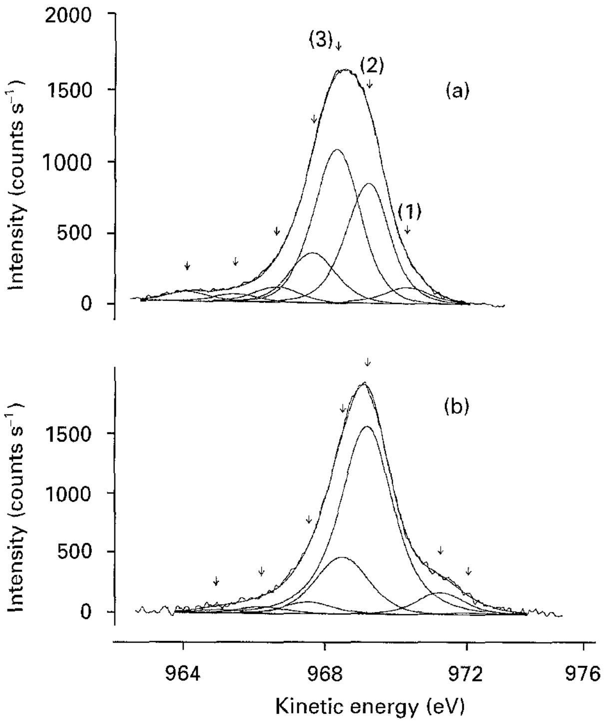

*Figure 11* C 1s core level spectra of (a) untreated fibres, (1) SiC, (2) C sp$^2$, (3) C–H, (b) fibres treated in argon at 1570 K.

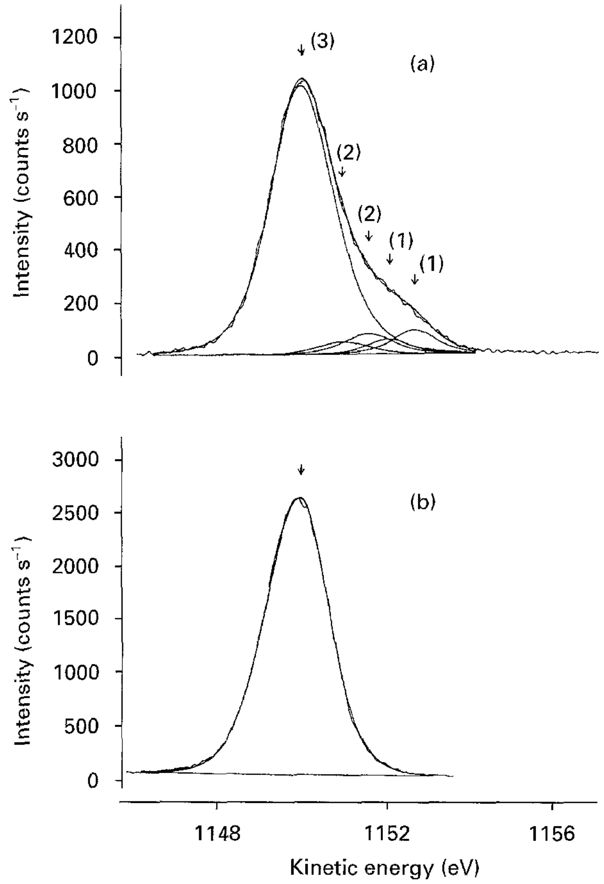

*Figure 12* Si 2p core level spectra for (a) untreated fibres, (1) SiC, (2) $SiO_xC_y$, (3) $SiO_2$, (b) fibres treated in argon at 1570 K.

deposition of volatile aluminium species from the alumina tube and crucible.

### 3.3.2. Fibres treated in argon

The spectra obtained after thermal treatment in argon are different from those established under vacuum (Figs 11 and 12). The C 1s core-level spectrum indicates that a well-organized carbon phase is present at the surface (Fig. 11). Independently from the treatment temperature, the Si 2p core-level spectra reveal the presence of an important silica layer because the other constituents of the fibre are not detected (Fig. 12). This explains the reactivity behaviour of the fibre after treatment in argon being comparable to the untreated fibre.

## 4. Discussion

The experimental results show that the chemical composition of the fibre undergoes important modifications in a vacuum at a temperature equal to or higher than 1470 K. To explain these chemical changes, the following reactions may be considered

$$2SiO_2 + SiC \rightarrow 3SiO + CO \qquad (6)$$

$$SiO + 2C \rightarrow SiC + CO \qquad (7)$$

Combining Reactions 6 and 7 one obtains

$$SiO_2 + 3C \rightarrow SiC + 2CO \qquad (8)$$

Thermodynamic calculations indicate that Reaction 8 can take place in the considered temperature range, 1270–1570 K, and in a reduced atmosphere, i.e. for a pressure of $CO < 0.7$ Pa, as measured experimentally. For Reaction 6, it was assumed that the pressure of SiO is three times higher than that of CO, as indicated by the reaction stoichiometry and under these conditions the free energy of Reaction 6 is also negative. It is obvious that SiO is overestimated in this calculation, but a lower pressure of SiO tends to decrease the free energy even further. Considering the molar composition of the fibre (0.16 mmol SiC, 0.94 mmol C, 0.42 mmol $SiO_2$) per gram and assuming that all free carbon reacts with silica according to Reaction 8 and the remaining part of silica with silicon carbide according to Reaction 6, the total weight loss of the fibre would be equal to 26%. This value is close to that found after thermal treatment of the fibre under vacuum at 1570 K of the fibre (25%).

In view of the reactivity measurements and the XPS results, it appears that the treatment of the fibre above 1270 K under vacuum leads to two important chemical modifications at the surface of the fibre: (i) the disappearance of the silica layer initially present at the fibre surface, (ii) the formation of a compound deficient in oxygen. First, the silica layer initially present at the surface is no longer detected by XPS for fibre treated at 1470 and 1570 K (Fig. 9). The disappearance of this layer is attributed to its reaction with SiC according to Reaction 6. As a result of the reaction between SiC and $SiO_2$, free carbon is accumulated on the surface during treatment above 1270 K (50 $\mu$mol g$^{-1}$ instead of 25 $\mu$mol g$^{-1}$ for untreated fibres). Kinetic limitations may probably explain the accumulation of free carbon which could react with SiO according to Reaction 7. Disproportionation of SiO may also take place

$$2SiO \rightarrow SiO_2 + Si \qquad (9)$$

which could also explain why free carbon is left unreacted on the fibre surface. The calculation of the free energy of Reaction 9 shows that it takes place at 1200 K under our experimental conditions (SiO pressure = 0.1 Pa). The presence of solid SiO formed at high temperature, which is converted to $SiO_2(s)$ and Si(s) on cooling, has been already mentioned by several authors [11, 19]. The mixture ($SiO_2$ + Si) may then easily react with oxygen at 1170 K and leads to the formation of $SiO_2$. This would explain why oxygen chemisorption on the fibre is in excess of the stoichiometry of SiC oxidation ($R < 1$) for samples heat treated at 1470 and 1570 K. Furthermore, XPS measurements have shown that the formation of silica takes place upon oxygen chemisorption of the fibre heated at 1570 K (see Fig. 10).

## 4.1. Fibres treated under vacuum

The results of oxygen chemisorption and XPS measurements lead to the following schematic representation of the SiC-based fibre heat treated at 1470 K under vacuum (Fig. 13). Three compounds are present: silicon carbide, free carbon and oxygen-deficient silica. The mean thickness of the superficial layer where oxygen-deficient silica is present may be estimated from the amount of fixed oxygen during sequence II (140 $\mu$mol g$^{-1}$) (see Fig. 5). Hence, considering the specific surface area of the fibre (0.11 m$^2$ g$^{-1}$) and the silica density (2.2) one obtains a mean thickness of about 30 nm. This value indicates that the degradation of the fibre at 1470 K is limited to a small but detectable surface layer. XPS measurements, however, indicate that the surface of the fibre is mainly constituted of SiC and carbon. Hence the oxygen-deficient silica compound is probably not detected by XPS. Beneath this perturbed layer, the overall composition of the fibre remains unaffected, because the ratio $R$ is still equal to 1.6. Consequently, after thermal treatment in vacuum at 1470 K the fibre has already a noticeable skin–core structure. This degradation mechanism is also observed at 1270 K. Indeed, a small amount of CO is measured during the treatment in vacuum at 1270 K indicating that decomposition is already taking place.

A schematic representation of the chemical composition is also given for the fibre heat treated at 1570 K under vacuum (Fig. 14). SiC, free carbon and oxygen-deficient silica are also found at the surface of the fibre heat treated at 1570 K. It is noticed, however, that the oxygen-deficient silica compound reacts now immediately with oxygen. The superficial layer where these three compounds are present has a mean thickness of about 30 nm, because 140 $\mu$mol g$^{-1}$ oxygen are chemisorbed at the end of the second sequence (see Fig. 5). This value is similar to that calculated at 1470 K. Furthermore, the surface of the heat-treated fibre has a higher rugosity and/or porosity. In contrast to treatment at 1470 K, the degradation process goes further beneath the perturbed layer as revealed by the high weight loss at 1570 K (see Table I) and the important amount of released CO. Indeed, the reactivity measurements show that the composition of the fibre is close to stoichiometric SiC (see Fig. 5, sequence III). Consequently, silica and free carbon have been almost totally consumed as expected if one considers a

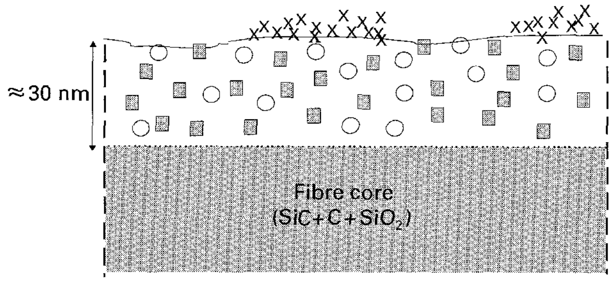

*Figure 13* Schematic representation of the chemical composition of SiC-based fibres heated under vacuum at 1470 K: (×) free carbon, (□) silicon carbide, (○) oxygen-deficient silica compound.

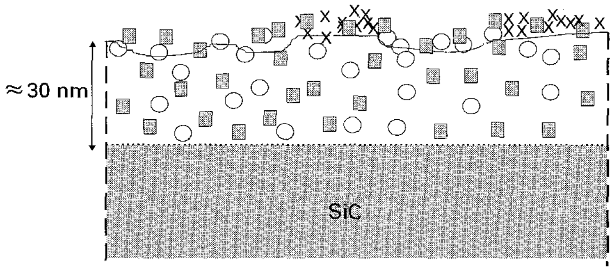

*Figure 14* Schematic representation of the chemical composition of SiC-based fibres heated under vacuum at 1570 K: (×) free carbon, (□) silicon carbide, (○) oxygen-deficient silica compound.

complete degradation of the fibre according to Reactions 6 and 8.

## 4.2. Fibres treated in argon

The treatment in argon is essentially characterized by the formation of an important silica layer at the surface of the fibre, as indicated by the XPS spectra (Fig. 12). The degradation process seems to be limited, as indicated by the weak weight loss after treatment in argon (see Table I). It is noticed that the pressure of oxygen present in argon is not high enough to involve a passive oxidation of SiC but can react with SiO on the fibre surface. Moreover, the fibres heat treated in argon have similar chemical composition to the untreated one ($R = 1.6$ in all cases). In particular, the free carbon present in the fibre core is not consumed, as for the fibre heated in vacuum at 1570 K. Hence, the higher thermal stability in argon at atmospheric pressure is due to a less pronounced degradation of the fibre and to the formation of a silica layer which further hinders the release of CO and SiO from the fibre core.

## 5. Conclusion

Thermal treatments in an inert atmosphere (vacuum or argon) of SiC-based fibres lead to surface modifications. An important evolution of the chemical composition at the surface of the fibre takes place after the treatment under vacuum which strongly modifies its oxidation behaviour. In particular, it is observed that the surface of the fibre is mainly constituted of silicon carbide and oxygen-deficient silica. On the contrary, the treatment in argon leads to the formation of a silica layer at the surface of the fibre. Whatever the type of treatment, the evolution of the chemical composition of the fibre undoubtedly modifies the interface properties in a composite material.

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