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Reactivity of a C/SiC composite in water vapour

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Abstract

The reactivity at high temperature of C/SiC composites is studied in water vapour and is compared with the one in oxygen. In particular, the respective part of the carbon gasification and SiC oxidation in the oxidation of the composite was determined by using a method which combines gravimetrical and gas phase composition measurements. Experimental results point out that C and SiC in the composite are significantly oxidized in water vapour, the carbon gasification being widely predominant. It has been also shown that the oxidation of the SiC matrix is strongly enhanced in water vapour, but this is not sufficient for acting as an oxidation barrier. It appears that others parameters like the presence of microfissures, the non-homogeneous covering of the carbon material in the composite play also a very important role. The obtained experimental results were confirmed by SEM observations. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Composite; C/SiC; Mass spectrometry; Oxidation; Thermogravimetry

1. Introduction

Carbon/carbon composites are used in several various fields of application requiring strength, light weight and toughness, e.g. aerospace equipments, disk brakes, medical prothesis. Especially, they are outstanding candidate materials for use as high-temperature structural components. A serious drawback arises, however, as these composites are used in an oxidising environment since carbon in any form will react with oxygen, burning away rapidly at temperatures higher than 400°C. To overcome this problem, several coating materials have been studied for the protection of C/C composites: the most common being silicon carbide. In this case, the carbon matrix has been replaced partly or totally by SiC, the material is then referred to 'C/SiC composite'. SiC may be formed using the chemical vapour infiltration (CVI), a process derived from the well-known chemical vapour deposition.[1–3] The behaviour of different C/SiC composites in dry oxygen has already been extensively studied. It appears that it will strongly depend on the nature of the carbon and the SiC.[4–7]

Hence C and SiC will react in the composite with O_2 according to the following reactions:

$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)} \tag{1}$$

$$SiC_{(s)} + 3/2O_{2(g)} \rightarrow SiO_{2(s)} + CO_{(g)} \tag{2}$$

It must be noted that reaction (2) is valid only if the partial pressure of O_2 is high enough to have the passive oxidation regime.[8–10] In this case, the oxidation of SiC leads to the formation of a protective silica film which will further limit the oxidation of the carbide.

On the contrary, a volatile non passivating oxide is formed at sufficiently high temperatures and low partial pressure of oxygen according to:

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

Reaction (3) corresponds to an active oxidation behaviour characterized by a loss of weight.[9] In the frame of this work, the chosen experimental conditions should favour the passive oxidation of SiC which has been extensively described in the literature.[11,12] For a short oxidation time, it has been shown that the oxidation through a very thin oxide layer is controlled by the interface reaction kinetics. In this case, the thickness of formed silica versus time relationship is linear. For a

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thicker oxide layer (i.e. for large oxidation time), the weight gain follows a parabolic law as follows:

$$x^2 = Bt \tag{4}$$

where x is the oxide thickness, B is the parabolic rate constant and t is the reaction time. B is also related to the diffusion coefficient of the oxidising species.

There is a general believe that the permeation of molecular oxygen through the growing oxide layer is the rate controlling step for oxidation below 1720 K.[12,13] The reported activation energy value in this regime (around 120 kJ/mol) agrees well with the energy required for molecular oxygen permeation in fused silica as reported by Norton.[14] However, recent experimental results[15] strongly support the fact that atomic oxygen is the more likely candidate for the transported species in the oxidation of silicon.

In the C/SiC composite, the SiC matrix acts as an oxygen barrier for the carbon fibre due to the formation of SiO_2 during its oxidation. However, the behaviour of such a composite may also strongly depend on morphological properties and in particular on the presence of fissures in the external layer of the ceramic coating due to the mismatch of thermal expansion between the carbide and the carbon. Theses fissures provide paths through which oxygen can migrate toward the carbon reinforcement and react with it. As a result, the mechanical properties of the material will dramatically weaken. A survey of the literature indicates that several studies have been carried-out to solve the problem of chemical oxidation of the carbon. In particular, phosphate, borate and silicate based-glasses have been used to seal cracks in the ceramic matrix.[16] However, this method will limit the application of the composite in air at temperatures lower than 1473 K. The use of mullite ceramics has been also investigated since mullite may form a liquid phase able to close cracks and pores leading to an improvement of the oxidation resistance.[17] However, under thermal cycling conditions, a significant decrease of the oxidation resistance was observed due to the presence of the cracks in the SiC layer and the spallation of this layer. Nowadays, a more or less satisfactory protective coating has been found depending on several experimental parameters of the CVI process (temperature, time of exposure, formation of multilayers).[6,18,19]

While the behaviour of C/SiC in dry oxygen has been well studied, less information is available on the reactivity of such material in the presence of water vapour, which may be formed, in particular when hydrogen is used as a propulsive element in engines. In these experimental conditions, C and SiC will react at temperatures above 1200 K with water vapour according to the following reactions:

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)} \tag{5}$$

SiC also reacts with water vapour leading to the formation of a silica layer:

$$SiC + 3H_2O \rightarrow SiO_2 + 3H_2 + CO \tag{6}$$

CO may then react further according to the water-gas shift reaction at lower temperature:

$$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)} \tag{7}$$

There is a general agreement within the literature that water vapour enhances the oxidation rate of SiC in the passive regime and that the oxidation kinetics of SiC follows a parabolic law over a long period of oxidation, indicating that the reaction rate is controlled in a diffusion manner similar to the one in dry air.[20,21] However, there is some discordance concerning the origin and the magnitude of this enhancement. Moreover, the reactivity of SiC in water vapour will strongly depend on several factors like : the purity of the SiC material, the nature of impurities in the SiC material and/or the oxidation environment.[22–25]

Different explanations have been given in the literature concerning the enhancement of the SiC oxidation in wet air or in water vapour. For instance, it was suggested that water vapour plays a strong influence on the crystallisation of amorphous silica which is said to accelerate SiC oxidation by promoting devitrification.[26–28] By comparison with the oxidation of silicon (which also leads to the formation of a silica layer), Schiroky[29] has suggested that the formation of hydroxylic groups into the silica network due to the presence of water vapour in an oxygen steam produces a less dense silica film which allows for faster diffusion of oxidising species and/or reaction products. In fact, Doremus[30] states in the case of the Si oxidation that water is dissolved as molecules in the amorphous silica layer and subsequently reacts with the silicon–oxygen lattice to form Si–OH bonds. Moreover, it has been shown that B varies linearly with the partial pressure of water vapour. This supports the hypothesis that permeation of molecular water based on solubility and diffusion rate in the amorphous silica layer controls the Si oxidation rate, suggesting that water was the major oxidant.[31] The diffusion coefficient of water in silica is an order of magnitude smaller than that of oxygen. However, the solubility of water in vitreous silica is a factor of 1000 larger than that of oxygen.[31,32] Therefore, the increased oxidation of Si in H_2O is attributed to the high solubility of H_2O in amorphous SiO_2. Recently, Opila [23] has also proposed a model for the oxidation of SiC in which the diffusion of molecular H_2O and charged species, such as OH^-, may both control the oxidation rate of SiC. It has been also mentioned that the oxidation mechanism of SiC in a H_2O/O_2 mixture is not really different from the one obtained in the H_2O/argon mixture. A slight difference may be, however, observed in the oxidation rate of SiC. This is not surprising since it has been shown by Opila that for an oxidation at 1470 K in an oxidizing mixture with a water content higher than 2.5%, the oxidation rate of SiC is controlled by the water-vapour permeability in silica rather than by the oxygen. Moreover, a higher oxidation rate of SiC may be also attributed to the catalytic effect of impurities.[22] Consequently, it is rather difficult to discriminate between the effects of water vapour and impurities. In particular, surface contamination of the sample may lead to a modification of the microstructure of the formed silica layer.[24,31] It has been shown that species coming from the reaction tube in alumina may also affect the oxidation kinetics, the scale composition and morphology of SiC. However, if care has been taken in isolating the effect of impurities, the oxidation rate of SiC in water vapour appears to be enhanced at temperatures of 1370–1470 K by about an order of magnitude over the rate observed in oxygen. Recently, it has been suggested that the silica layer that is formed on SiC during the oxidation in water vapour may be volatile under some conditions.[33]

Hence, there is a general agreement that an atmosphere containing water vapour is more corrosive than a dry one to SiC formed by CVD.

The objective of the present work is to study the behaviour at high temperature of a C/SiC composite in water vapour. A comparison with its reactivity in oxygen is also undertaken. The behaviour of the composite in oxidising environment may be forecast from the knowledge of the reactivity in the composite of SiC and C which both may be oxidised. It must be noted that the gasification of carbon induces a weight loss of the sample. On the contrary, the oxidation of SiC leads to a weight gain of the material. Therefore, the overall weight variation of the composite taking place during the oxidation process may be positive or negative depending on which reaction (carbon gasification or SiC oxidation) is predominant. As commonly described in the literature, this weight variation of the material during the oxidation may be measured by thermogravimetry analysis (TGA). However, it appears that the major drawback of this technique is the measurement of an *overall* weight variation which makes it impossible to distinguish the carbon gasification from the SiC oxidation. A differentiation between C and SiC oxidation may be achieved by taking in account the change in gas phase composition during the oxidation of the composite. Indeed, reactions (5) and (6) indicate that the respective amounts of evolved CO and H_2 are different in the case of C and SiC. Hence, a combination of gravimetrical and gas phase composition measurements should allow the determination of the respective part of C and SiC in the oxidation process.

2. Experimental

2.1. Materials

The studied material denominated as 'C/SiC composite' is constituted by a carbon component (60% by volume of the final composite) and silicon carbide as matrix. The carbon component of the composite consists of PAN-based carbon fibres impregnated by a phenolic resin. The carbon prepreg has been further carbonized at 900°C. The resulting carbon material is then further densified by chemical vapour infiltration (C.V.I.) using a mixture of CH_3SiCl_3 and H_2. C/SiC discs (10 mm in diameter and 1.5 mm in thickness) are then cut in the densified material. These discs are then covered by a CVI–SiC layer before running the oxidation tests. The specific surface area of the composite (measured by krypton adsorption at 77 K) is equal to 0.6 m^2/g.[34]

Oxidation experiments were also conducted separately on PAN-based carbon fibres and the SiC matrix. The SiC matrix was obtained after gasification of a C/SiC composite in air at 900°C. The resulting silica was removed by dissolution in hydrofluoric acid before the oxidation test. The specific surface area of SiC matrix measured by gas adsorption is equal to 1.2 m^2/g.

2.2. Oxidation procedure

The investigated C/SiC material (0.25 g) is deposited in an alumina crucible and introduced in a fused silica reactor. The system is then heated in an argon flow at atmospheric pressure up to 1170 or 1470 K. As the desired temperature is reached, the oxidising mixture (argon/water vapour) or (argon/oxygen) is then admitted into the reactor. The partial pressure of argon in both mixtures is equal to 80 kPa. Water vapour is produced by a vapour generator and its inlet partial pressure is 20 kPa. The oxidant gas flows at 6 l/h from the bottom of the reaction tube over the sample up to the top of the reactor, where it is continually conveyed with a capillary tube to a quadripolar mass spectrometer (Leybold Quadrex 200) for a quantitative analysis of the gas phase. Prior to experiment, the mass spectrometer has been calibrated with pure gases (H_2, CO, CO_2 and O_2; purity better than 99.995%). A counter flow of 6 l/min dry nitrogen was circulated through the balance chamber to prevent water condensation in the microbalance. In the case of the oxidant gas containing H_2O, the gas phase collected at the top of the furnace goes first through a (water/ice)-cooled condenser in order to trap the unreacted water vapour which would otherwise disturb the quantitative analysis by mass spectrometry.

For example, the determination of the composition of the gas phase resulting from the oxidation of the carbon fibres taken separately will allow to follow their reactivity in a way similar to the study by gravimetry analysis.

As an illustration, the results obtained by mass spectrometry for the oxidation of carbon fibres by water vapour at 1470 K are shown in Fig. 1. It can be observed that the gas phase is mainly constituted by hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2) which correspond to the products of reactions (5) and (7). It appears in Fig. 1 that the amount of gas formed during the oxidation increases almost linearly with time. Additional experiments have confirmed that CO_2 comes from the reaction between CO and water vapour [reaction (7): water–gas shift reaction] taking place in the cooler zone of the furnace. Hence, the total number of mol of gasified carbon Nt(C) corresponds to the sum of the number of mol of CO and CO_2 as represented in Fig. 1. In the same manner, the number of mol of hydrogen resulting from reaction (5), N(H_2), can be deduced from the total number of mol of hydrogen measured by mass spectrometry. The change of N(H_2) is also shown in Fig. 1. It clearly appears that the evolution of Nt(C) is similar to the one of N(H_2) indicating that the determination of the composition of the gas phase is fairly accurate.

For gravimetrical measurements, the crucible containing the sample is linked to a microbalance (Mettler AE240) in order to follow the overall weight variation of the material as a function of oxidation time. The variation of the mass of consumed carbon measured by gravimetry during the oxidation of carbon fibres is represented in Fig. 2. It can be seen that after 1.5 h of reaction, the whole amount of carbon has been consumed. For comparison, the weight change of the same sample calculated from the Nt(C) data obtained by mass spectrometry is also shown in Fig. 2. It appears that there is a satisfactory agreement between the results given by mass spectrometry and by gravimetry. The observed difference corresponds to experimental uncertainties which lie within 10%. The same trend has been found when N(H_2) is considered for the calculation of the amount of carbon gasified instead Nt(C). Therefore, further calculations will be only based on Nt(C).

It has been verified that similar results have been obtained in the case of the oxidation of the carbon fibres in oxygen. The experiment carried-out with the carbon fibres permits the validation of the method combining mass spectrometry and gravimetry which is forecast to be used in the case of composite C/SiC.

2.3. Material characterisation

Morphological changes of the composite during oxidation are observed by scanning electron microscopy. External and inner parts of the composite have been examined on transverse sections cut from the sample with a diamond saw. Electron dispersive spectroscopy (EDS) has been also investigated on the observed samples.

3. Results and discussion

3.1. Reactivity of C/SiC composite in water vapour at 1470 K

An overall weight variation is measured by gravimetry during the oxidation of the composite at 1470 K in presence of water vapour as shown in Fig. 3. It can be seen that after an initial period characterised by a very limited weight loss and which lasts for about 15 min, the weight of the sample decreases in a significant manner. The measurement of a weight loss which represents about 8 wt.% of the initial weight of the material after 7 h of experiment indicates that carbon gasification is the predominant reaction.

H_2, CO and CO_2 are the main gases detected during the oxidation as shown in Fig. 4. As already mentioned for the oxidation of carbon fibres, CO_2 is originated from the water–gas shift reaction (7). Therefore, one

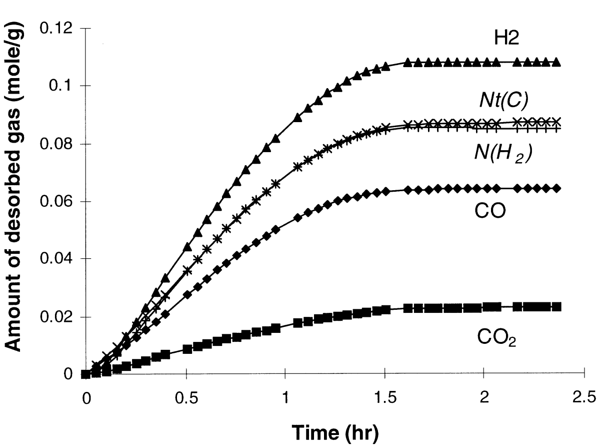

Fig. 1. Amount of desorbed gas vs time for the oxidation of carbon fibres by water vapour at 1470 K.

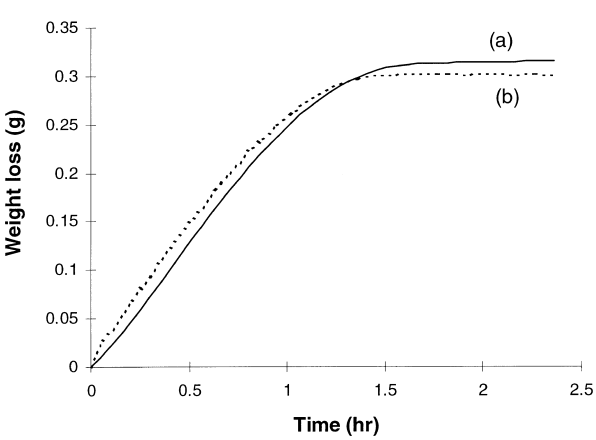

Fig. 2. Weight loss vs time for the oxidation of carbon fibres by water vapour at 1470 K (a) gravimetry measurements, (b) mass spectrometry measurements.

defines $\mathrm{Nt}_{(CO)}$ which is the total number of formed CO according to reactions (5) and (6) and taking reaction (7) into account. The change of $\mathrm{Nt}_{(CO)}$ vs time is represented in Fig. 4. It can be seen that $\mathrm{Nt}_{(CO)}$ increases almost linearly during the whole experiment.

To determine the respective reactivity of SiC and C in the composite, the calculations described above have to be followed:

- The oxidation of SiC leads to a weight gain of the sample, $\Delta \mathrm{m}_{(SiC)}$, which corresponds to:

$$\Delta m_{(\mathrm{SiC})} = m_{(\mathrm{SiO2})} - m_{(\mathrm{SiC})} \tag{8}$$

where $m_{(\mathrm{SiO2})}$ and $m_{(\mathrm{SiC})}$ corresponds to the amount of formed SiO_2 and of consumed SiC respectively.

Considering the stoichiometry of reaction (6) and the molar mass of SiO_2 (60 g) and SiC (40 g), Eq.(8) can be written as:

$$\Delta m_{(\mathrm{SiC})} = 20^{*} N_{(\mathrm{SiC})} \tag{9}$$

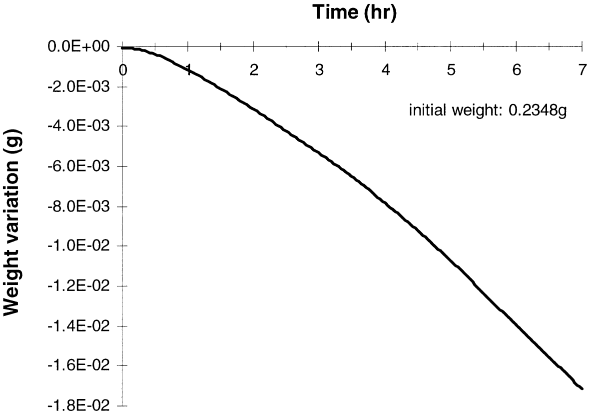

Fig. 3. Overall weight variation vs time for oxidation of the C/SiC composite at 1470 K by water vapour.

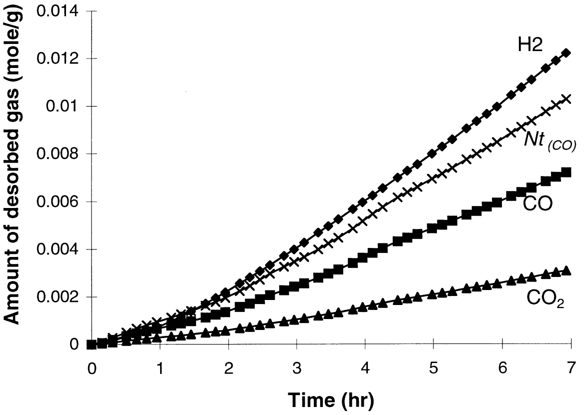

Fig. 4. Amount of desorbed gas vs time for oxidation of the C/SiC composite at 1470 K by water vapour.

where $N(_{\mathrm{SiC}})$ is the number of mol of SiC consumed according reaction (6).

- The gasification of carbon leads to a weight loss, $\Delta m_{(\mathrm{C})}$, of the sample.

Considering reaction (5), one obtains:

$$\Delta m_{(\mathrm{C})} = 12^{*} N_{(\mathrm{C})}$$

where $N_{(\mathrm{C})}$ is the number of mol of gasified carbon.

The overall weight variation (Δm) which is measured by gravimetry follows the relationship:

$$\Delta m = \Delta m_{(\mathrm{SiC})} - \Delta m_{(\mathrm{C})} \tag{10}$$

that is to say:

$$\Delta m = 20^{*} N_{(\mathrm{SiC})} - 12^{*} N_{(\mathrm{C})} \tag{11}$$

Moreover, considering reactions (5) and (6), $N_{(\mathrm{SiC})}$ and $N_{(\mathrm{C})}$ may be related to $Nt_{(\mathrm{CO})}$ determined by mass spectrometry since

$$Nt_{(\mathrm{CO})} = N_{(\mathrm{C})} + N_{(\mathrm{SiC})} \tag{12}$$

Finally, from Eqs. (11) and (12), the amounts of consumed carbon and silicon carbide during the oxidation of the composite may then be deduced. The following equations are then obtained:

$$m_{(\mathrm{C})} = 0.375^{*}\left(20^{*} Nt_{(\mathrm{CO})} - \Delta m\right) \tag{13}$$

$$m_{(\mathrm{SiC})} = 1.25^{*}\left(\Delta m + 12^{*} Nt_{(\mathrm{CO})}\right) \tag{14}$$

Consequently, from the last two equations, the weight loss due to carbon gasification and the weight gain attributed to the SiC oxidation in the composite as a function of oxidation time may be computed as seen in Fig. 5. This figure shows the measured changes of C/SiC

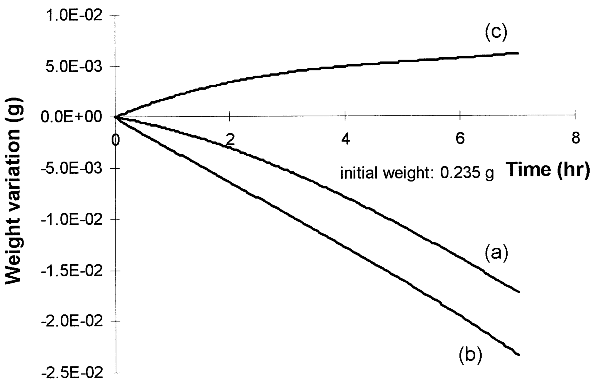

Fig. 5. Oxidation of C/SiC composite by water vapour at 1470 K; (a) overall weight variation, (b) weight loss due to carbon gasification, (c) weight gain due to SiC oxidation.

sample oxidized at 1470 K by water vapour (initial weight: 0. 235 g) and the corresponding calculated weight loss for C and weight gain for SiC. It can be seen that both components, carbon prepreg and silicon carbide matrix, significantly contribute to the evolution of the material during the oxidation. Considering that the material consists of 60% by weight of carbon, the obtained results indicate that 17 wt.% of C and 13 wt.% of SiC have been consumed after 7 h at 1470 K. The rather important fraction of gasified carbon indicated that the protective effect of SiC is limited in these oxidation conditions.

The oxidation of the SiC matrix is significant as indicated in Fig. 5. For a reaction time larger than 1 h, the oxidation of the matrix follows a parabolic kinetics since a linear form is obtained when the weight gain due to SiC oxidation squared is plotted versus time (Fig. 6). The value of the parabolic rate constant (*B*) determined from this plot is equal to 3.2×10^{-4} g^2 h^1 m^4. In the case of the oxidation in the same conditions of a SiC sample of same size but without carbon prepreg (see experimental part), the oxidation rate of SiC is much higher leading to a value of *B* equal to 10.2×10^{-3} g ^{2} h^1 m^4 as shown in Fig. 6. An important discrepancy is observed between both values of *B*. This difference may be explained by the fact that water vapour will preferentially react with carbon in the composite and consequently the fraction of available SiC for reaction with water vapour is reduced.

The obtained experimental results point out that a rather important fraction of carbon is gasified inside the composite. More informations have been brought by SEM examinations of the composite before and after oxidation. In fact, SEM views of the external surface of the initial composite (Fig. 7) indicate that microcracks are present in the SiC layer which is characteristic of CVI–SiC. This is not really surprising since it is known that the CVI–processing of the C/SiC composites generates mechanical stresses in the material when cooling to room temperature as the result of differential thermal expansion. Hence these microcracks form an appropriate pathway for the oxidising species and consequently may favour the gasification of the carbon reinforcement. Moreover, transverse sections of the composite were also observed by SEM (Fig. 8). It appears that for the initial composite, carbon fibres are almost totally covered by the matrix which is constituted on C and SiC [Fig. 8(a)]. After oxidation, the layer which initially covered the carbon fibres is almost completely oxidised [Fig. 8(b)]. In the case of the present work, the disappearance of this layer may be only attributed to the oxidation of the phenolic-based carbon layer. This observation also indirectly suggests that the CVD–SiC matrix is not distributed homogeneously in the composite since its oxidation would lead to the formation of a silica layer. Therefore, it may be deduced that the presence of microcracks and the non-uniform covering of the carbon prepreg by the SiC matrix will strongly favour the accessibility of the oxidising gas toward the carbon. These observations are consistent with the significant weight loss measured for the composite oxidation by water vapour.

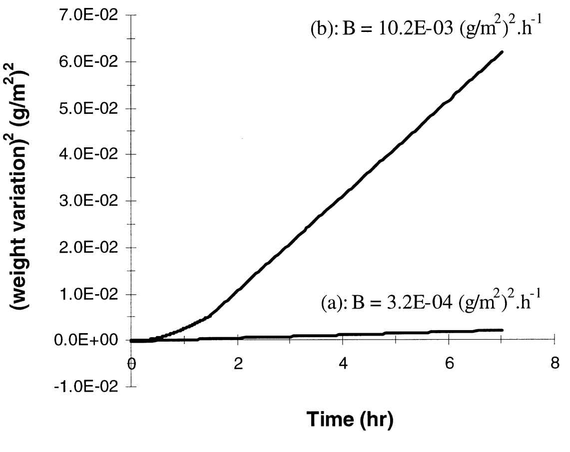

Fig. 6. Weight gain squared vs time-oxidation at 1470 K by water vapour of (a) C/SiC composite, (b) SiC without carbon material.

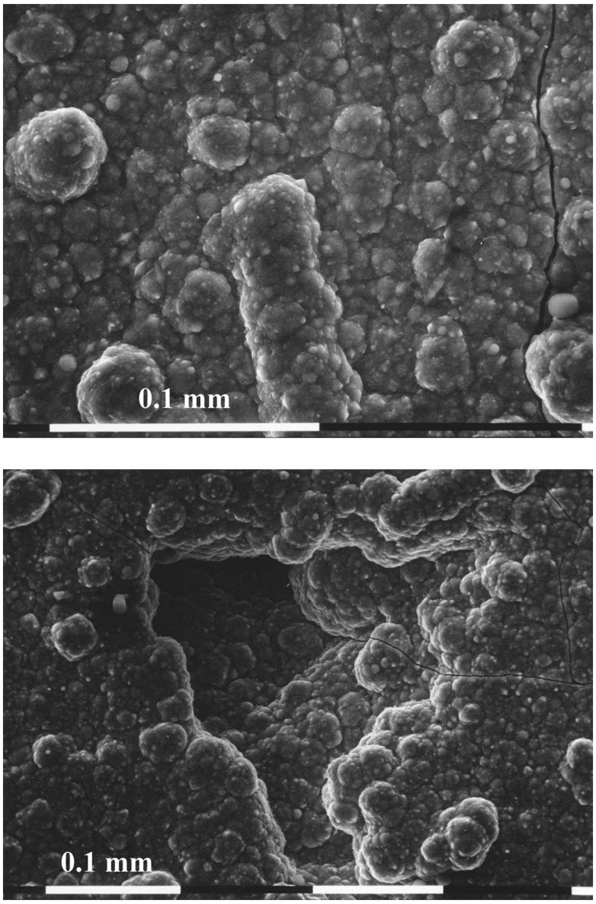

Fig. 7. SEM views of the external surface of the C/SiC composite.

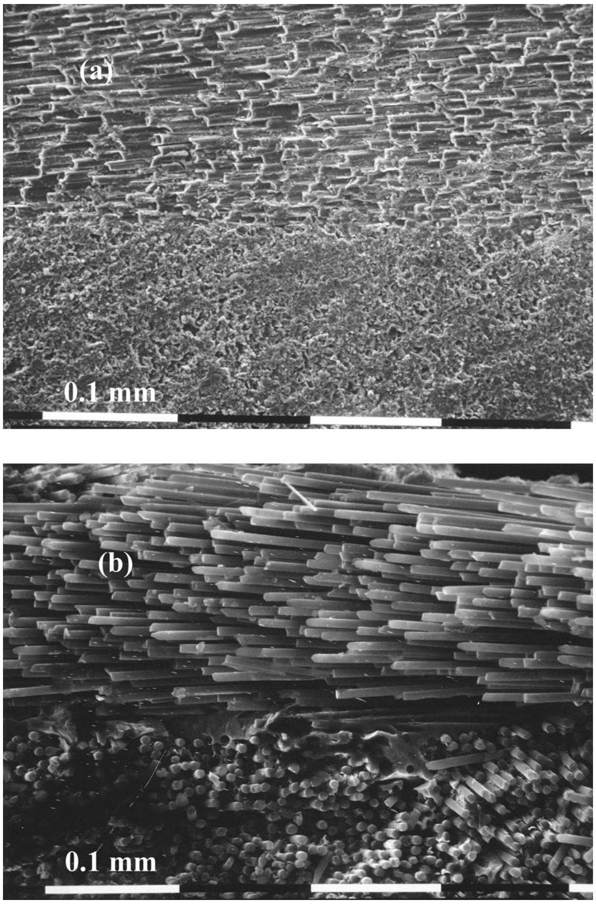

Fig. 8. Transverse section of the C/SiC composite: (a) initial composite, (b) composite oxidized 7 h by water wapor at 1470 K.

3.2. Reactivity of C/SiC composite in oxygen at 1470 K

Oxidation in oxygen was also carried-out and the results were compared to those obtained in water vapour. The weight changes of the composite and the composite components in oxygen at 1470 K are shown in Fig. 9. It can be observed that the whole amount of carbon is consumed after 35 h of experiment. As for the oxidation in water vapour, the gasification of carbon seems to be the predominant reaction. An oxidation regime for SiC is observed after 32 h of reaction, i.e. when the weight gain becomes significant. Therefore for $t > 32$ h, the value of the constant B was determined and compared to the one calculated in the case of the oxidation of a disc without prepreg as seen in Fig. 10. It appears that the values are closed (1.1×10^{-4} g^2 h^1 m^4 for SiC disc and 0.9×10^{-4} g^2 h^1 m^4 for SiC in the composite). Such a trend is consistent with the fact that SiC oxidation becomes noticeable only when the whole carbon has been consumed.

A transverse section of the material after oxidation has been observed by SEM (Fig. 11). The uncomplete empty tubes observed in this view are constituted of SiC and SiO_2, the last resulting from the oxidation of SiC.

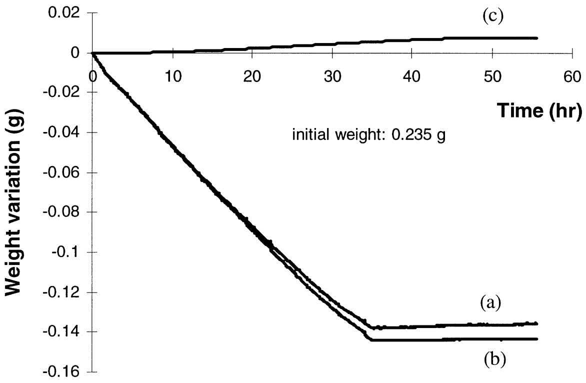

Fig. 9. Oxidation by oxygen at 1470 K: (a) overall weight variation, (b) weight loss due to carbon gasification, (c) weight gain due to SiC oxidation.

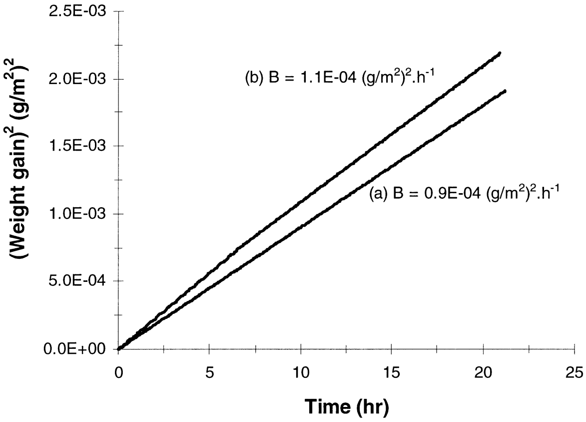

Fig. 10. Weight gain squared vs time: oxidation at 1470 K by oxygen of (a) C/SiC composite, (b) SiC without carbon material.

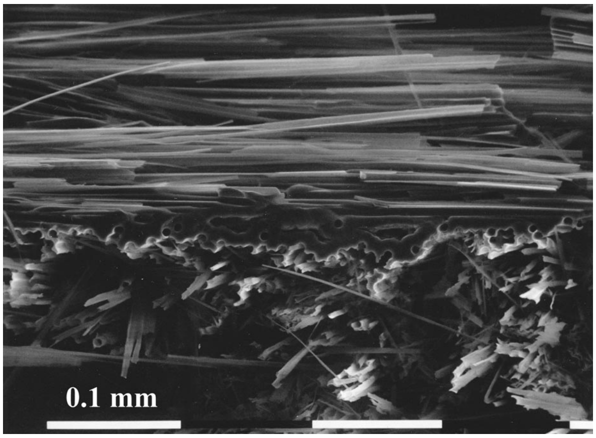

Fig. 11. Section of the composite after oxidation by oxygen at 1470 K.

Moreover, the presence of these uncomplete tubes confirm that the SiC matrix does not uniformly cover the carbon fibres. Similar to the observations made in water vapour, the presence of microcracks and the fact that the SiC matrix is not uniformly distribute on the carbon

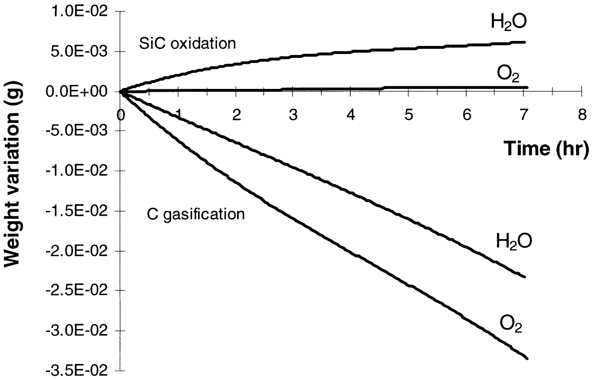

Fig. 12. Reactivity of C and SiC in the composite by water vapour and oxygen at 1470 K.

fibres is probably responsible for the important gasification of the carbon material.

It is more interesting to compare the reactivity of SiC and C in the composite in water vapour and oxygen after 7 h of reaction in order to have a more precise description of the behaviour of the composite in both the oxidising environment (Fig. 12). It is seen in this figure that SiC oxidation is strongly enhanced in water vapour. This result is confirmed by the values of the parabolic rate constant (Figs. 6 and 10). In particular, the ratio [B (in water vapour)/B (in oxygen)] is equal to 68 and 3.5 for the SiC disc and the SiC in the composite respectively. However, it must be noted that the magnitude of enhancement in water vapour is much more higher than the one mentioned in the published data.[12,17,18] This may be attributed to the fact that the studies mentioned in the literature mainly concern a very pure rectangular sample of CVD–SiC and not a SiC sample originated from a final composite material like in this study. In particular, it is clear that the potential presence of impurities in the composite will undoubtedly modify the kinetics of the oxidation. The lower value of the ratio in the case of the composite results from the presence of the carbon material which react with the oxidising environment and, therefore, reduces the SiC reactivity.

The gasification of the carbon material is significant in both oxidising environment as seen in Fig. 12. Moreover, carbon material is more rapidly gasified in oxygen than in water vapour which is the reverse situation to the one observed for the SiC reactivity. Consequently, the amount of consumed carbon after 7 h of reaction is higher by a factor 1.6 as compared to the one measured in water vapour. The lower reactivity of the carbon material in water vapour may result from (i) the formation of a noticeable silica layer due to SiC oxidation which further acts as an oxygen barrier. This 'self healing' behaviour has already been observed for other type of composite;[7,35,36] (ii) the decrease of the gasification rate of the carbon prepreg due to the formation of the gases CO, H_2 which act as inhibitors for reaction (5). This has been already mentioned in previous work.[37]

Table 1
Oxidation rate in oxygen and water vapour of carbon fibres and of carbon fibres in composite

Material	$r_C(O_2)$ (%/h)	$r_C(H_2O)$ (%/h)
Carbon fibres	227	136
Carbon material in the composite	3.5	2.3

The reactivity of the carbon prepreg was also compared to the one of carbon fibres. Oxidation rates at 15% of burn-off are determined as indicated in Table 1. The oxidation rate for the C material was deduced from the carbon reactivity data [Fig. 12(b)]. As expected, the gasification rate of carbon material in the composite is much lower than the one of carbon fibres due to the presence of the SiC matrix. A ratio (gasification rate of carbon fibres/gasification rate of the carbon material in the composite) was determined in order to estimate the protective effect of the matrix for both oxidising gases. Results which are reported in Table 1 indicate that the highest protective effect is observed in oxygen since the values of ratio are equal to 70 and 50 in oxygen and water vapour respectively. This may be attributed to the physico-chemical modifications of the formed silica layer which induces a higher solubility of water vapour in silica and consequently a higher concentration of oxidising gas around the carbon.

4. Conclusion

The studied C/SiC composite is very sensitive to oxygen and water vapour. It was possible using a method which combines mass spectrometry and gravimetry to determine the respective part of the carbon gasification and SiC oxidation in the oxidation of the composite. In this way, it appears that the gasification of the carbon material is the predominant reaction in O_2 and H_2O. The role playing by SiC as a oxidation barrier seems to be limited although its oxidation is noticeable in H_2O. This may be partly attributed to the fact that SiC does not uniformly cover the carbon prepreg and to the presence of microfissurations.

The satisfactory results obtained in the frame of this study could be used for investigating the reaction of other types of composite materials.

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