



HAL
open science

High temperature oxidation of SiC f /PyC/SiC composite in helium for the Gas-cooled Fast Reactor

Ludovic Charpentier, Marianne Balat-Pichelin, Kamel Dawi, F. Audubert

► **To cite this version:**

Ludovic Charpentier, Marianne Balat-Pichelin, Kamel Dawi, F. Audubert. High temperature oxidation of SiC f /PyC/SiC composite in helium for the Gas-cooled Fast Reactor. 8th INTERNATIONAL SYMPOSIUM ON HIGH-TEMPERATURE CORROSION AND PROTECTION OF MATERIALS, May 2012, Les Embiez, France. hal-02313875

HAL Id: hal-02313875

<https://hal.science/hal-02313875>

Submitted on 11 Oct 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

High temperature oxidation of SiC_f/PyC/SiC composite in helium for the Gas-cooled Fast Reactor

Ludovic Charpentier^a, Marianne Balat-Pichelin^a, Kamel Dawi^a, Fabienne Audubert^b

^a PROMES-CNRS, 7, rue du Four Solaire, 66120 FONT-ROMEUE ODEILLO, France

^bCEA, DEN, DEC/SPUA/LTEC, CEA Cadarache, 13108 SAINT PAUL LEZ DURANCE, France

Ludovic.Charpentier@promes.cnrs.fr;Marianne.Balat@promes.cnrs.fr; fabienne.audubert@cea.fr

Abstract. The cladding material envisaged for the Gas-cooled Fast Reactor (GFR) is a SiC_f/PyC/SiC composite with a β-SiC coating on the surface that is subjected to temperatures going up to 1500 K in nominal operating condition and up to 2300 K in accidental operating conditions, in helium pressurized at 7 MPa. An experimental approach was made on SiC_f/PyC/SiC under active oxidation conditions ($1400 \leq T \leq 2300$ K; $0.2 \leq p_{O_2} \leq 2$ Pa). The variation of the mass loss rates according to the temperature showed the existence of three domains. The oxygen partial pressure had a weak impact on the mass loss rate for temperatures lower than 2070 K. Beyond 2070 K, the mass loss rate increased leading to important damage of the material, at lower temperature under $p_{O_2} = 0.2$ Pa than under $p_{O_2} = 2$ Pa, which was associated to the effect of the oxygen partial pressure on the sublimation of SiC.

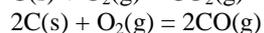
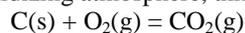
Keywords: SiC, composites, oxidation, characterization

INTRODUCTION

The cladding material that is envisaged for the Gas-cooled Fast Reactor (GFR), one of the systems belonging to the 4th Generation of nuclear systems, is a composite material made of silicon carbide fibers (SiC_f) surrounded by a SiC matrix deposited through chemical vapor infiltration (CVI), both elements being separated by a pyrocarbon (PyC) thin interphase. The surface of this composite is covered using chemical vapor deposition (CVD) by a layer of β-SiC, in order to reduce the penetration of oxidizing species as demonstrated by Lamouroux *et al.* [1]. Inside the GFR, the coolant is helium gas at total pressure of 7 MPa. It is planned to support temperatures up to 1500 K in nominal conditions. Nevertheless, in case of a pressure drop of the coolant, the temperatures can quickly increase up to 2300 K (accidental conditions).

In such nominal and accidental conditions, SiC could be oxidized by the oxygen impurities of the coolant according to two regimes. The passive one occurs under low temperature or high oxygen partial pressure, with the formation of a silica layer (SiO₂), protecting the material from further oxidation. When the temperature increases or the oxygen partial pressure decreases, the oxidation becomes active, with the release of gaseous SiO and more important damage of the material as no more silica layer prevents the oxygen from reaching the SiC material.

The main problem of the current SiC/SiC composite is the presence of a pyrocarbon interphase (PyC). In oxidizing atmosphere, this interphase is consumed according to the following reactions:



In the case of thin interphase ($< 0.1 \mu\text{m}$), the vacuum thus created can be filled with silica, fragile and adherent. A study on the behavior and oxidation mechanism of the SiC/SiC composites with conventional pyrocarbon interphase (PyC-SiC/SiC) and advanced multi-layer interphase (ML-SiC/SiC) using thermogravimetric analysis (TGA) in He-O₂ atmosphere at 1270 and 1470 K was carried out recently [2]. Both the PyC-SiC/SiC at 1470 K and the ML-SiC/SiC at 1270 and 1470 K presented a relatively low mass change during the oxidation. This was

associated to relatively fast growth of silica on the SiC matrix and fibers, closing the access of oxidizing species before the beginning of the carbon combustion. In the case of PyC-SiC/SiC oxidized at 1270 K, significant mass loss rate was measured, associated with a too slow growth of silica to close the porosity and to avoid a PyC recession.

This study focuses on the oxidation behavior of SiC/PyC/SiC composite with β -SiC coating at high temperature (1400-2300 K) and in helium atmosphere with reduced oxygen partial pressure (0.2 and 2 Pa). The solar high temperature and pressure reactor (*Réacteur Hautes Pression et Température Solaire*, REHPTS) enables to reproduce very fast temperature increase (up 100 K s⁻¹) up to this high temperature level. This work follows two preceding studies carried out on two polytypes of SiC: α and β under the same conditions [3, 4] where the influence of the crystalline structure on the passive/active transition temperature and on the mass loss rate was discussed. In this publication, we focus on the oxidation behavior of SiC/PyC/SiC at the temperature range of nominal operation and in the case of incident or accident for GFR. The mass loss kinetics under accidental operating conditions, the behavior and the lifetime of the cladding are discussed. Various techniques of analysis (SEM, XRD, mass spectrometry, etc.) were used to interpret the results.

EXPERIMENTAL PROCEDURE

The oxidation tests were performed using the High Pressure and Temperature Solar Reactor (REHPTS) facility formerly described [3, 5]. This reactor installed at the focus of the 5 kW solar furnace allows studying the behavior of materials subjected to high temperatures in controlled atmosphere with increase temperature speed ranging from 10 to 100 K s⁻¹ similar to those that may occur during an incident or accident in a nuclear reactor.

The oxidation tests were conducted on a SiC/PyC/SiC composite developed by Snecma Propulsion Solide (SPS). This material consists of a β -SiC matrix produced by CVI (Chemical Vapor Infiltration) and reinforced by Hi-Nicalon fibers (β -SiC) with a pyrocarbon interphase (PyC). A β -SiC coating deposited by the CVD (Chemical Vapor Deposition) method on one face is used to close the porosity of the surface.

To reproduce the possible atmospheres of the GFR, different helium qualities from Air Liquide were used: He Alphagaz1 with 2 ppm O₂ and 1 ppm H₂O and He U with 20 ppm O₂, with a gas flow of 10 l min⁻¹. Samples were oxidized during 10 min at constant temperatures ranging from 1400 to 2300 K. The heating rate up to the plateau is between 20 and 100 K s⁻¹ and the cooling down to the room temperature is about 20 K s⁻¹. The total pressure inside the REHPTS is maintained at 10⁵ Pa.

The samples are weighed before and after oxidation in order to calculate the relative mass changes. SEM imaging was performed to analyze the surface morphology.

Some samples were pre-oxidized during 48 h at 1300 K in ambient air inside an electrical furnace to develop a silica layer before being treated inside the REHPTS in helium with pO₂ = 2 Pa, in order to define the effect of a silica layer on the active oxidation kinetics.

RESULTS AND DISCUSSION

Oxidation experiments and surface characterization

Table 1 summarizes the experimental conditions of the various tests carried out on β -SiC-SiC/PyC/SiC composites under pO₂ = 0.2 and 2 Pa, and the corresponding mass variations, given in mg cm⁻² min.

Figure 1 presents the pictures of some representative samples of SiC/PyC/SiC oxidized under pO₂ = 0.2 and 2 Pa. Temperature measurement was performed on a 6mm-diameter circle in the center of each sample. We notice three different surface morphologies according to the oxidation temperature: (1) a representative surface for passive oxidation (samples oxidized at 1540 K) looking like the initial state, (2) a surface presenting a limit state between passive oxidation and active oxidation (samples oxidized at 1650 K) and (3) a surface more damaged representative of active oxidation (samples oxidized at 1970 and 2200 K). We observe on the samples oxidized at 2200 K the existence of greenish zones representative of areas more attacked than the remainder of the sample.

TABLE 1. Summary of the tests carried out on β -SiC-SiC/PyC/SiC composites oxidized in Helium at P = 1 atm, according to the temperature and pO₂ and oxidation regime and reported mass change rates

Temperature (K)	pO ₂ = 0.2 Pa		pO ₂ = 2 Pa	
	Oxidation regime	Mass change rate	Oxidation regime	Mass change rate

		($\text{mg cm}^{-2} \text{ min}^{-1}$)		($\text{mg cm}^{-2} \text{ min}^{-1}$)
1540	Passive	0.02	Passive	- 0.01
1650	Passive/active	0.00	Passive/active	- 0.03
1740			Active	- 0.06
1850	Active	- 0.04		
1970	Active	- 0.14	Active	- 0.09
2030	Active	- 0.23	Active	- 0.23
2070	Active	- 0.36		
2100	Active	- 0.68	Active	- 0.39
2130	Active	- 0.78		
2160			Active	- 0.44
2190			Active	- 1.10
2200	Active	- 1.33	Active	- 1.59
2220			Active	- 0.69
2250			Active	-2.06

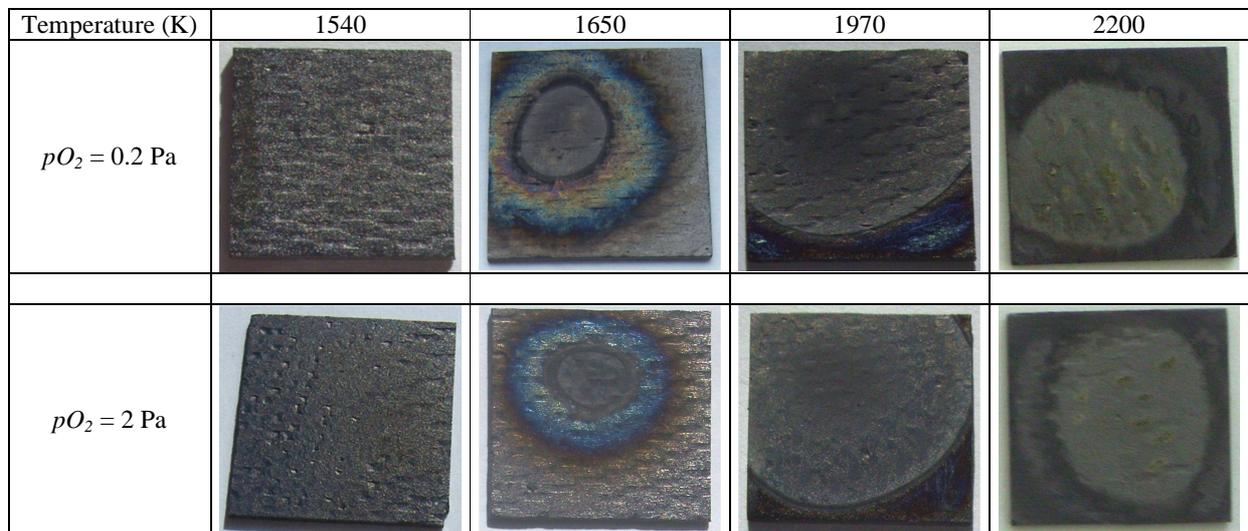


FIGURE 1. Pictures of β -SiC-SiC/PyC/SiC composites after oxidation under $pO_2 = 0.2$ and 2 Pa at different temperatures.

Figure 2 shows the SEM images and the oxidation regime of characteristic samples of β -SiC-SiC/PyC/SiC oxidized under $pO_2 = 2 \text{ Pa}$. We can see in the images: (a) the surface of the reference sample, (b) the presence of a silica layer characteristic of passive oxidation, (c) a limit state between passive (silica crystals and needles appearing as white) oxidation and active (grey parts with a lot of holes) oxidation and for the other samples, (d) (e) and (f), the presence of a surface increasingly attacked which is characteristic of active oxidation. It may be noticed that in the case of active oxidation, various surface states are observed according to the temperature level. Indeed, for samples oxidized under active oxidation conditions at 'moderate' temperatures - samples (d) - the surface appears covered with small grains and rather rough, while for samples oxidized at higher temperatures - sample (f) - the surface appears in this case smooth with large grains with several porosities. We note that a limit case between these two ones is observed on the sample (e). The same observations were noted in the case of $pO_2 = 0.2 \text{ Pa}$.

We can see that by increasing the temperature, the surface appears more attacked with a larger porosity emerging on the surface. The replacement of small grains by larger grains is observed from 2070 K under $pO_2 = 0.2 \text{ Pa}$, and from 2100 K under $pO_2 = 2 \text{ Pa}$. This replacement may be related to the coalescence of grains at high temperature, coupled with consumption of small grains by sublimation.

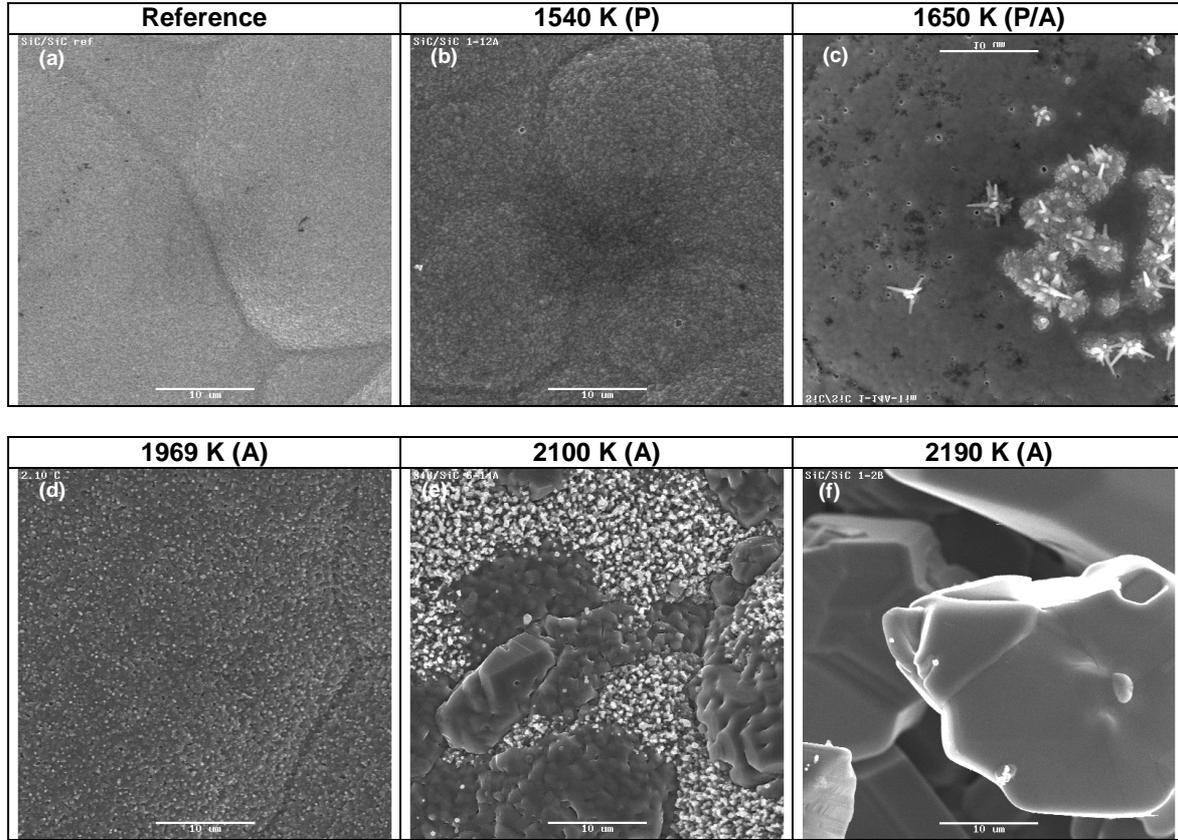


FIGURE 2. SEM images of the surface of β -SiC-SiC/PyC/SiC composite before (a) and after oxidation under $pO_2 = 2$ Pa at 1540 K (b), 1650 K (c), 1970 K (d), 2100 K (e) and 2190 K (f).

Kinetics of active oxidation

Figure 3 shows the evolution of the mass loss rate versus temperature for β -SiC-SiC/PyC/SiC oxidized under $pO_2 = 0.2$ and 2 Pa. These variations of the mass loss rate are calculated in $mg\ cm^{-2}\ min^{-1}$ by taking into account the total front surface of the sample.

This representation gives a clear vision of the impact of temperature on the mass loss rate. There are three domains in the active oxidation regime for the two oxygen partial pressures. In the case of $pO_2 = 0.2$ Pa, we observe a linear and low mass loss rate up to 1970 K, domain (I), then a significant increase of the mass loss rate in two steps, domains (II) and (III). The domain (II) shows a mass loss rate increasing 4 times higher than that of the domain (I), whereas the domain (III) shows that the mass loss rate is increasing 3.6 times higher than that of the domain (II). The equations of linear trends are the following ones with the corresponding correlation coefficient (v in $mg\ cm^{-2}\ min^{-1}$ and T in K):

- domain (I)	$1670 \leq T \leq 1970\ K$	$v = 0.0005\ T - 0.79$	$(R^2 = 0.85)$
- domain (II)	$1970 \leq T \leq 2070\ K$	$v = 0.0020\ T - 3.88$	$(R^2 = 0.97)$
- domain (III)	$2070 \leq T \leq 2200\ K$	$v = 0.0073\ T - 14.71$	$(R^2 = 0.98)$

In the case of $pO_2 = 2$ Pa, the corresponding linear trends are the following ones with the corresponding correlation coefficient (v in $mg\ cm^{-2}\ min^{-1}$ and T in K):

- domain (IV)	$1650 \leq T \leq 1970\ K$	$v = 0.0002\ T - 0.24$	$(R^2 = 0.94)$
- domain (V)	$1970 \leq T \leq 2160\ K$	$v = 0.0019\ T - 3.68$	$(R^2 = 0.97)$
- domain (VI)	$2160 \leq T \leq 2250\ K$	$v = 0.0156\ T - 33.14$	$(R^2 = 0.61)$

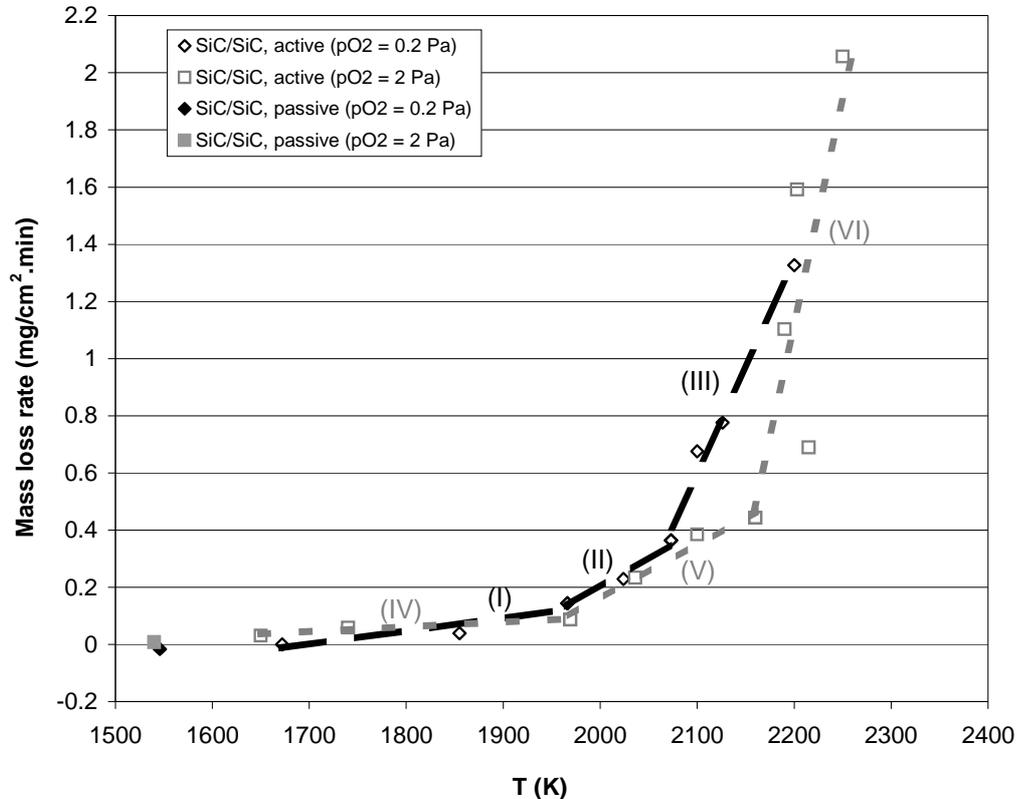


FIGURE 3. Comparison between the mass loss rates according to temperature for SiC/PyC/SiC oxidized under $pO_2 = 0.2$ and 2 Pa.

The increase of the mass loss rate is more important under $pO_2 = 2$ Pa than the one calculated under $pO_2 = 0.2$ Pa. Thus, the mass loss rate of the domain (V) is 9.5 times more important than that of the domain (IV) and the mass loss rate of the domain (VI) is 8 times more important than that of the domain (V).

To explain this first increase of the mass loss rate, we refer to the observations of the transverse cross-sections on figure 4. Indeed, the SEM micrograph of the sample in domain (V) (at 2160 K, figure 4 (d)) reveals a surface matrix detached from the body of the composite with a more important degradation of the β -SiC coating compared to the intact matrix and β -SiC coating observed in the case of the reference sample (figure 4 (a)) and in the case of the domain (IV) samples (e.g. samples oxidized at 1540 and 1740 K, figure 4 (b) and (c)). Thus, the body of the composite is more and more exposed to the oxidizing atmosphere and a very damaging oxidation is taking place which is characterized by an increase of the mass loss rate. Same observations were noticed in the case of the samples oxidized under $pO_2 = 0.2$ Pa.

Above 2160 K for $pO_2 = 2$ Pa and 2070 K for $pO_2 = 0.2$ Pa, the sublimation of SiC(s) to Si(g), Si₂C(g) and SiC₂(g) may start at this temperature leading to an important mass loss rate [6]. This sublimation reaction explains the greenish zones observed on the surface of the samples exposed to very high temperatures (Figure 1, samples at 2200 K). The SEM observations of transverse cross-sections carried out on these zones show that the β -SiC coating has nearly completely disappeared, along with an advanced oxidation of the matrix (figure 4 (e) and (f)). This advanced degradation, preferentially on some zones of the surface, can be explained by a SiC layer (matrix + coating) more or less thick according to irregular surface roughness of the composite. A longer exposure under these conditions will lead to a total revealing of the body of the composite. In addition, the chemical analyses performed by EDS in these greenish zones and gray areas around them showed, in both cases, a typical composition of SiC.

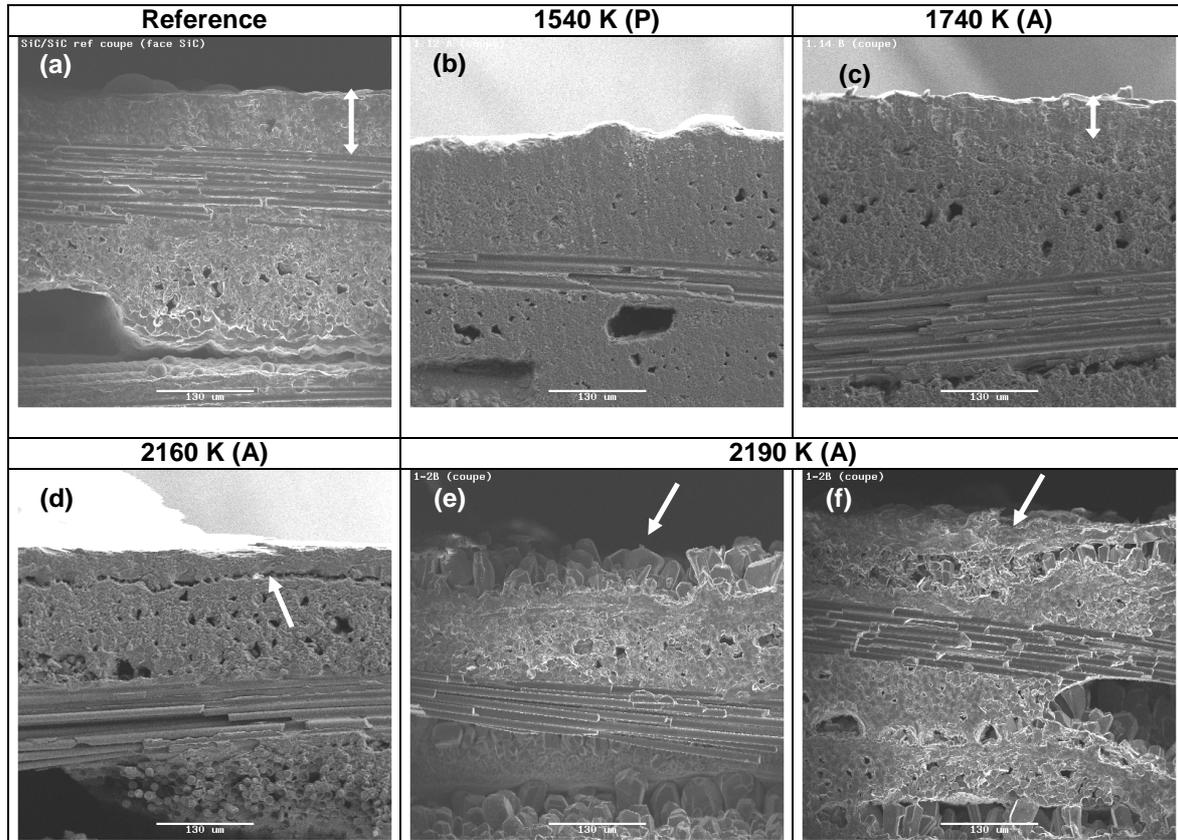


FIGURE 4. SEM images of transverse cross-sections of SiC/PyC/SiC before (a) and after oxidation under $pO_2 = 2$ Pa at 1540 K (b), 1740 K (c), 2160 K (d) and at 2190 K (observation in the level of a greenish zone (e) and of a grey zone (f))

These results show, for temperatures lower than 2070 K, the weak impact of oxygen partial pressure (in the range 0.2 - 2 Pa) on the mass loss rate of material. Beyond 2070 K, the composite SiC/PyC/SiC shows an increase in the degradation rate. This increase occurs at a lower temperature for $pO_2 = 0.2$ Pa than for $pO_2 = 2$ Pa. This difference could be associated with the increase of the SiC sublimation temperature according to pO_2 [6].

Oxidation study on the uncoated face

In order to study the role of the β -SiC coating, several oxidation tests were also performed under incidental and accidental operating conditions on SiC/PyC/SiC samples on the uncoated face. Table 2 summarizes the various tests conducted under $pO_2 = 2$ Pa.

TABLE 2. Summary of the tests carried out on the uncoated face of SiC/PyC/SiC composite under $pO_2 = 2$ Pa, temperature conditions and mass change rate

T (K)	Mass change rate (mg/cm ² .min)
1760	- 0.04
1970	- 0.20
2130	- 0.42
2180	- 0.61
2200	- 0.61
2220	- 1.03

Figure 5 shows the evolution of the mass loss rates versus temperature for β -SiC-SiC/PyC/SiC oxidized under $pO_2 = 2$ Pa. The empty circles represent the results obtained on the uncoated face. We note in this case, the existence of two oxidation domains in the zone of active oxidation. The equations of linear trends are the following ones with the corresponding correlation coefficient (v in $mg\ cm^{-2}\ min^{-1}$ and T in K):

- domain (VII) $1760 \leq T \leq 2170$ K $v = 0.0013 T - 2.28$ ($R^2 = 0.92$)
- domain (VIII) $2170 \leq T \leq 2220$ K $v = 0.0083 T - 17.58$ ($R^2 = 0.65$)

Compared to the results obtained on the samples oxidized on the coated face, the results obtained on the uncoated face show a linear mass loss rate between 1760 and 2170 K, which strongly increases beyond 2170 K due to the sublimation of SiC at very high temperature.

The mass loss rates and the SEM observations do not show a great influence of the β -SiC coating on the oxidation behavior of β -SiC-SiC/PyC/SiC at high temperature. This coating which seems to be too thin (as shown by the SEM observations of transverse cross-sections) in case of accidental conditions of the GFR (active oxidation) remains essential to close the porosity of the surface and to prevent a direct contact between the reactant gases and the body of the composite. This can explain the linear trend of mass loss rate between 1760 and 2205 K obtained on SiC/PyC/SiC oxidized from the uncoated face due to direct internal oxidation of the body of the composite, compared to the mass loss rate in two stages observed on SiC/PyC/SiC oxidized from the coated face.

Study on pre-oxidized samples

Table 3 summarizes the experimental conditions for tests carried out on SiO_2 - β -SiC-SiC/PyC/SiC pre-oxidized during 48 hours in air at 1300 K, and the corresponding mass variations, given in percentage and $mg\ cm^{-2}\ min^{-1}$. According to temperature, the SEM observations of the oxidized samples show a change in the surface morphology from a surface covered with small grains to a smooth surface composed of large grains. This change occurs at temperatures around 2170 K like in the case of the non-pre-oxidized samples.

TABLE 3. Summary of the tests carried out pre-oxidized SiO_2 - β -SiC-SiC/PyC/SiC composite under $pO_2 = 2$ Pa, temperature conditions and mass change rate

T (K)	Mass change rate ($mg/cm^2.min$)
1760	- 0.04
1890	- 0.08
2160	- 0.91
2170	- 0.38
2210	- 0.72

The solid squares on Figure 5 represent the tests carried out on the pre-oxidized samples. The equations of linear trends which take into account these points together with the ones obtained on non pre-oxidized samples are the following ones with the corresponding correlation coefficient (v in $mg\ cm^{-2}\ min^{-1}$ and T in K):

- domain (IX) $1650 \leq T \leq 1970$ K $v = 0.0002 T - 0.24$ ($R^2 = 0.94$)
- domain (X) $1970 \leq T \leq 2160$ K $v = 0.0016 T - 3.07$ ($R^2 = 0.90$)
- domain (XI) $2160 \leq T \leq 2250$ K $v = 0.0140 T - 29.80$ ($R^2 = 0.54$)

It can be seen, by comparison between the results obtained on pre-oxidized samples with those on normal samples, that the presence of a silica layer on the surface, formed after pre-oxidation in air during 48 hours, does not affect the kinetics of active oxidation in accidental conditions. For the GFR, it is clear that the formation of SiO_2 during the nominal operation mode is stabilized after a certain duration. The silica layer thus formed remains very thin and volatilizes very quickly in the case of accident at high temperature and consequently does not protect the material from aggravated active oxidation.

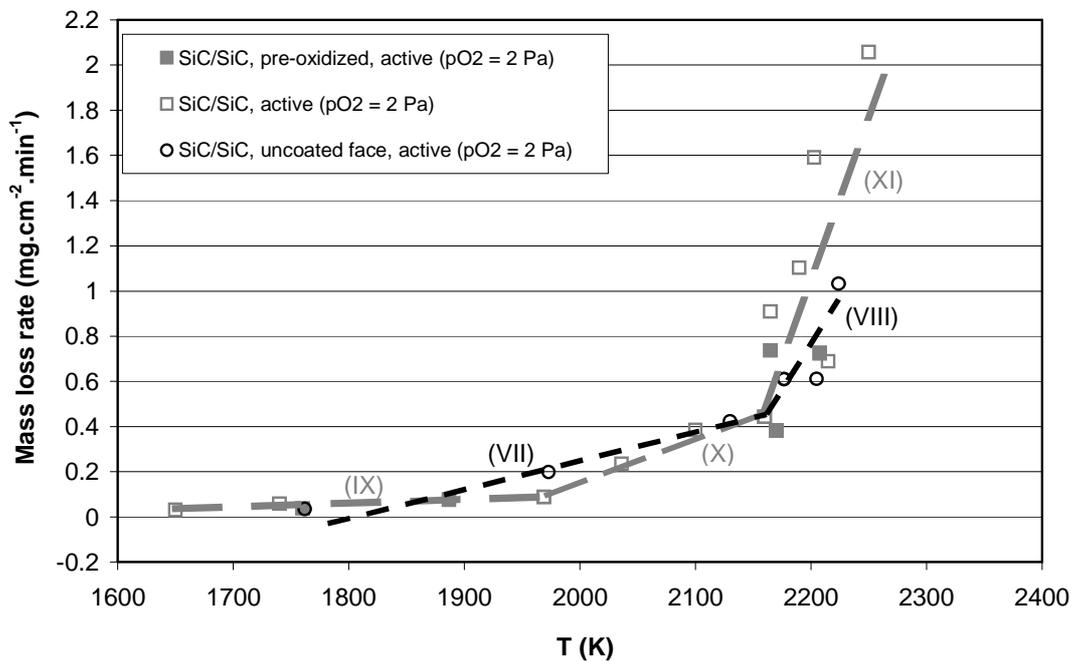


FIGURE 5. Evolution of the mass loss rate versus temperature for β -SiC-SiC/PyC/SiC oxidized under $p_{O_2} = 2$ Pa. The empty circles represent the tests performed on SiC/PyC/SiC composite oxidized from the uncoated face and the solid squares represent the tests performed on pre-oxidized SiO₂- β -SiC-SiC/PyC/SiC samples.

CONCLUSION

The experimental study carried out on the β -SiC-SiC/PyC/SiC composites has enabled to determine the oxidation rates under incidental and accidental operating conditions for two low oxygen partial pressures, 0.2 and 2 Pa in a total helium pressure of 1 atm. The evolution of mass loss rates versus temperature shows the existence of three domains in the active oxidation regime. These tests have also shown the weak impact of oxygen partial pressure on the mass loss rate - in the range 0.2-2 Pa - for temperatures below 2070 K. Beyond 2070 K, we notice an increase of the mass loss rate at lower temperatures for $p_{O_2} = 0.2$ Pa than for $p_{O_2} = 2$ Pa. This difference was associated with the effect of oxygen partial pressure on the sublimation temperature of SiC.

For the tests carried out on the uncoated face, the results do not show a great influence of the β -SiC coating on the oxidation behavior at very high temperature. This coating which seems to be too thin for accidental conditions remains essential to prevent a direct contact between the reactant gases and the body of the composite.

The variation of mass loss rate do not show a great importance of SiO₂ layer formed after pre-oxidation. This layer will not protect the SiC/PyC/SiC in accidental operating conditions.

REFERENCES

1. F. Lamouroux, G. Camus and J. Thébault, *Journal of the American Ceramic Society*, **77**, 2049 (1994).
2. S. Wu, L. Cheng, L. Zhang, Y. Xu and Q. Zhang, *Materials Science & Engineering B*, **130**, 215 (2006).
3. L. Charpentier, M. Balat-Pichelin and F. Audubert, *Journal of the European Ceramic Society*, **30**, 2653 (2010).
4. L. Charpentier, M. Balat-Pichelin, H. Glénat, E. Bêche, E. Laborde and F. Audubert, *Journal of the European Ceramic Society*, **30**, 2661 (2010).
5. L. Charpentier, M. Balat-Pichelin, D. Sciti and L. Silvestroni, *this conference*.
6. K. Dawi, M. Balat-Pichelin, L. Charpentier and F. Audubert, *Journal of the European Ceramic Society*, **32**, 485 (2012).