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SiC/SiC COMPOSITE BEHAVIOR IN LWR CONDITIONS AND UNDER HIGH TEMPERATURE STEAM ENVIRONMENT

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ABSTRACT

Tubular nuclear-grade SiC/SiC composites produced by CEA were investigated in the present work as cladding material to enhance the accident tolerance of Light Water Reactors (LWRs). A first part reports a preliminary assessment of the behavior of SiC/SiC composite tubes in simulated relevant LWR conditions related with the manufacturing parameters. The dependence of the corrosion rate on the chemical composition of water is also investigated for a better understanding of the hydrothermal SiC corrosion mechanisms. Additionally, the ability of SiC/SiC composite tubes to preserve their geometry and maintain coolability under high temperature steam environment is examined. Oxidation tests are performed to confirm the favorable behavior and to evaluate the oxidation kinetics of the composite exposed to high-temperature steam (up to 1400°C) under pressure and under dynamic gas flow conditions.

1. Introduction

The growing interest for continuous SiC fiber reinforced SiC matrix composites (SiC_f/SiC) as structural material for nuclear applications has resulted in significant improvements over the past decade. Primarily driven by the functional specifications of the fuel cladding element for fast breeder reactors, an important R&D program has led the French Alternative Energies and Atomic Energy Commission (CEA) to propose several innovations to overcome some critical technological issues [1]. Following the event at Fukushima in 2011, these innovative materials are now being seriously considered to enhance the accident tolerance of Light Water Reactors (LWRs). This development is being performed within the French Nuclear Institute in partnership with AREVA and EDF.

Due to their benefits over the conventional zirconium alloys such as low oxidation rates up to about 1600°C and presumably significant reduction in hydrogen generation, the application of SiC/SiC claddings to LWRs would provide favorable perspectives in emergency situation. The “sandwich” cladding design that includes a metal liner in between two layers of composite appears as a robust and technically viable concept [2,3].

The current development phase focuses on assessing the behavior under conditions representative of LWRs. Among the first technical attributes to be investigated is the resistance to corrosion, and other interactions with the coolant in LWR nominal operating conditions. Regarding this issue, the relative attractiveness and benefits of a SiC-based cladding remain to be demonstrated experimentally. Similarly, given the nature of LWR accidents, the study must also be extended to the high temperature steam behavior assessment. These two aspects constitute one of the major directions for current researches at CEA.

This paper addresses preliminary results quantifying and discussing the performance of tubular nuclear grade SiC/SiC composite materials in both normal and accident conditions.

2. Materials and experimental details

Specimens evaluated in this study included SiC/SiC composite tubes without metallic liner of 60 mm lengths. Hi-Nicalon™ type S reinforcements were used for their high purity and near stoichiometric composition (ratio Si/C~1) that confer stability under neutron irradiation. The tubular fibrous preforms were obtained either by an only-braiding process using a multi-path machine or by the association of both filament winding and 2D braiding processes to produce multilayered architectures. They were chemically vapor-infiltrated with a single pyrocarbon (PyC) interphase thickness of less than 100 nm. Outer diameter of tubes was about 10 mm with 0.85 to 0.90 mm wall thickness. To investigate the effect of oxidation on damaged composites, some specimens were intentionally pre-damaged at different level of interest (0.05 %, 0.1 %, 0.3 % and 0.5 %) to generate a controlled micro-crack network in the matrix, thus facilitating the ingress of oxidizing species.

Two autoclaves were used to evaluate the oxidation in LWR nominal operating conditions for 3500 h (5 months). One contained distilled water (DW), the second contained LWR like water composition with Lithium, LiOH (2 ppm) and Boron, H₃BO₃ (1000 ppm). Constant temperature and pressure were respectively measured to be 360°C and 180 bar.

As for the accidental simulated experiments, double-sided oxidation exposures were conducted for 4 to 110 hours in steam and air or O₂ mixtures (given in Table 1) with various oxygen contents. Details of the high-pressure and high temperature experimental set-up are described elsewhere [4]. The investigated temperatures were 1200°C and 1400°C and the total pressure was 1 or 10 bar. The linear gas velocity was constant and set to 5 cm/s for all the experiments.

Table 1 – Conditions applied to specimens exposed under high temperature steam

Conditions		Temperature (°C)	Pressure (bar)				Pressure ratio (%)		
			Total	Water	Gas in addition		P _{H2O} /P _T	P _{O2} /P _T	P _{O2} /P _{H2O}
P _{atm}	A	1200	10	0.5	Air	9.5	0,05 (5)	0,19 (19)	3,8
	B	1200	1	0.5	O ₂	0.5	0,5 (50)	0,5 (50)	1
	C	1200	1	0.5	Air	0.5	0,5 (50)	0,1 (10)	0,2
	D	1400	1	0.5	Air	0.5	0,5 (50)	0,1 (10)	0,2

For both sets of experiments, specimen weight was measured before and after exposure using microbalance with ± 0.05 mg/cm² accuracy. Uniaxial tensile tests were performed at room temperature to evaluate the residual mechanical behavior. Additional characterizations included analyses of composition surface by X-ray photoelectron spectroscopy (XPS) and microstructural post-exposure observations on polished cross-sections by scanning electron microscopy (SEM).

3 Results

3.1 Oxidation in representative nominal LWR conditions

Normal operating conditions for LWRs (temperature and pressure) are related to the hydrothermal oxidation regime of silicon carbide [5]. Under these conditions in water-containing environment, pure silicon carbide materials would be expected to form a protective silica SiO_2 layer due to the thermodynamic driving force. But besides incurring oxidative reactions with water, solution of the oxidation product in the coolant must also be considered to be part of the process.

- **Weight change and chemical composition analysis of waters**

The results of experiments are compiled in tables 2 and 3. With the exception of one slightly pre-damaged tube, a weight loss is observed for all the tested SiC-based samples. The reference and the low pre-damaged SiC/SiC materials (up to 0.05 % strain) reveal a limited weight change while significant weight loss is mainly observed for SiC/SiC pre-damaged materials above 0.05 % strain, without being related to the level of pre-damage. This means that water infiltrates through the larger crack openings (resulting from highly pre-damaged composites) and oxidizes the SiC materials from the inside and not just on the surface, thus increasing the corrosion rate.

The appearance of samples stays unchanged before and after exposure. No influence of the water chemistry on weight change is evidenced. If the presence of a significant content of Al in solution after 5 months exposure is clearly due to the sample holder made of alumina, Cr, Fe and Ni elements in very low quantities comes from the stainless steel autoclave. By contrast, the presence of Si in solution with a concentration corresponding to water solubility limit of silica at 25°C (0,12 - 0,14 g.l^{-1}) suggests a release from the SiC-based samples.

Table 2 – Weight evolutions of high purity CVD β -SiC and CVI-SiC/SiC tubular composites.

	Distilled water			LWRs water		
	initial weight (g)	after oxidation (g)	relative change (%)	initial weight (g)	after oxidation (g)	relative change (%)
SiC/SiC _{REF}	4.2937	4.2912	- 0.06	4.2494	4.2472	- 0.05
SiC/SiC _{0.05%}	4,6114	4,6142	+ 0.06	4.4845	4.7853	+ 0.02
SiC/SiC _{0.10%}	4,8429	4,8075	- 0.73	4.8059	4.7624	- 0.91
SiC/SiC _{0.15%}	4,7344	4,6873	- 0.99	4.7553	4.7181	- 0.78
SiC/SiC _{0.30%}	4,9728	4,9442	- 0.58	4.8866	4.8647	- 0.45
SiC/SiC _{0.50%}	5,0001	4,972	- 0.56	5.0783	5.0534	- 0.49

Table 3 – Chemical composition analysis (and pH) of waters before and after exposure.

Elements	Distilled water		LWRs water	
	initial	after 5 months	initial	after 5 months
Al	< 0.50	8200	96	4500
Si	< 0.05	84	< 0.05	68
B	8.4	13	1010	970
Li	< 10^{-3}	0.86	1.95	0.51
Cr	< 0.03	1.2	< 0.03	30
Fe	< 0.1	13	< 0.1	18
Ni	< 0.05	8	0.22	45
pH	7.0	8.3	7.5	7.9

Compositions are expressed in ppb

- **Post-exposure mechanical tensile behavior**

Residual tensile tests were carried out on the SiC/SiC tubular specimens according to the procedure detailed in [6]. No significant degradation of mechanical behavior is observed after long-term exposure in environments either representative of LWRs or distilled water. The monotonic post-exposure stress-strain curves for the investigated conditions, shown in figure 1a with a comparison to the reference behavior, are characteristic of the expected damageable behavior with a low fiber-matrix bonding. This is the consequence of low interfacial shear strength due to the presence of pyrocarbon interphase, which does not seem to have been affected. The intentional pre-damage of specimens at different strain levels (0.05 to 0.5 %) to allow access of oxidizing species to the bulk material also exhibit a proper post-exposure mechanical behavior that consolidates this assumption (see figure 1b). The fiber-matrix load transfer remains efficient to provide ability to accommodate the deformation for the silicon carbide ceramic composites.

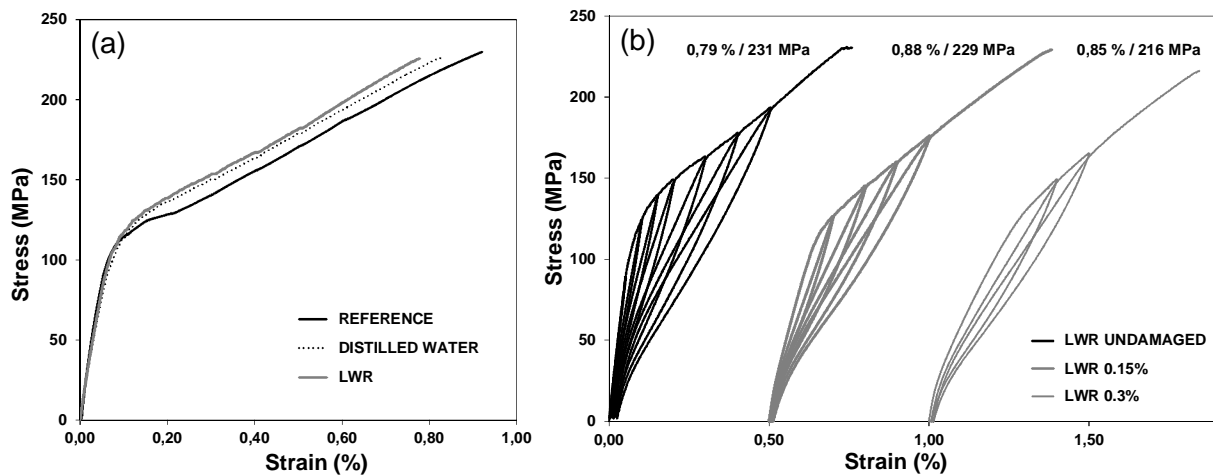
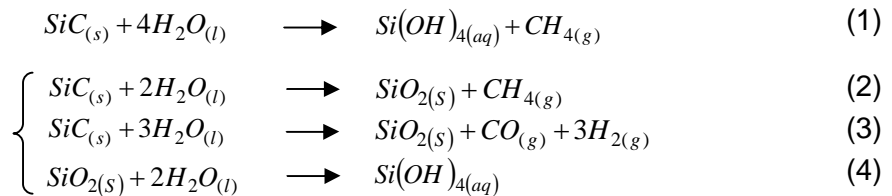


Fig. 1: (a) Post-exposure stress-strain curves in tensile of SiC/SiC composite specimens and comparison of with the reference curve (monotonic),
 (b) Unloading-reloading sequences to confirm the non-sensitivity of mechanical behavior on both as-received and pre-damaged specimens after long-term exposure in LWR environment – Values correspond to strain/stress at failure.

- **Discussion and mechanism**

Regarding these first results, the long-term exposure in autoclave of pure silicon carbide under environments characteristic of normal operating LWR conditions leads to a weight loss. Besides the possible active oxidation such as described by reaction (1), it could be assumed that material recession mainly results from the dissolution of the silica oxide formed initially on the surface and likely to form silicic acid in the aqueous state. Depending on the activity of the solid phases in presence and the water-to-SiC ratio, the sequence of thermodynamically consistent reactions (2) (3) (4) are thought to be possible [7-8]. In both cases, material is being consumed.

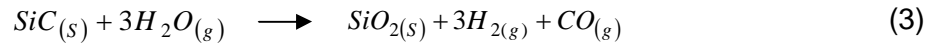
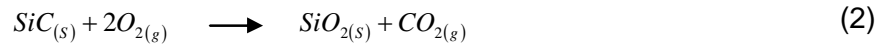
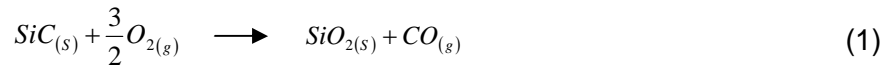


As reported by different authors, no evidence of protective silica layer was observed on silicon carbide nuclear grade material tested in similar conditions [5,9]. This result was confirmed in the present study by XPS analysis showing exposed surfaces free of silica scale.

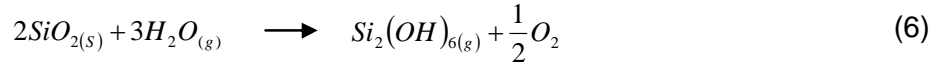
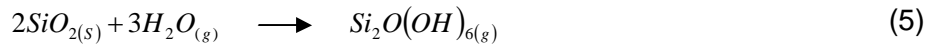
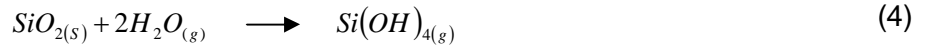
As soon as the silica oxide would form on the surface, it dissolves in the water. However, since solubility of silica depends on temperature, the silica dissolution could raise an issue in case of fuel cladding application as the possible silica particles would be transported through the coolant and then deposited in the colder parts of the power loop or pumps. In the meantime, the SiC-based cladding would undergo continuous thickness loss.

3.2 Oxidation in high temperature steam

The reference oxidation studies of SiC materials in high temperature steam environment have been carried out for needs related to aircraft turbine engine applications [10-11]. Under conditions such as combustion environments (high temperature, high pressure) containing oxygen with water vapor, it is well-established that the SiC oxidation reaction, which is temperature dependent, follows a parabolic oxidation kinetics. Material recession is governed by a two-step process of silica scale formation on the surface of SiC by any or all of the reactions (1) (2) (3) followed by volatilization of this generated oxide.



Water vapor is found to be the primary oxidant specie. It is directly involved in the volatilization of the silica scale to form volatile hydroxides or oxohydroxides that ultimately results in mass loss after relative long-term exposure. Some possible reactions (4) (5) (6) are the following:



By relying on this mechanism, a time series of specimens was performed to determine the oxidation reaction parameters. Figure 2 shows the results for CVI-SiC/SiC tubular composites exposed under various high temperature steam environments, as described in Table 1. The data points report the average and standard deviation of 3 weight change measurements, normalized to the exposed surface area of composites that was obtained by X-ray tomography.

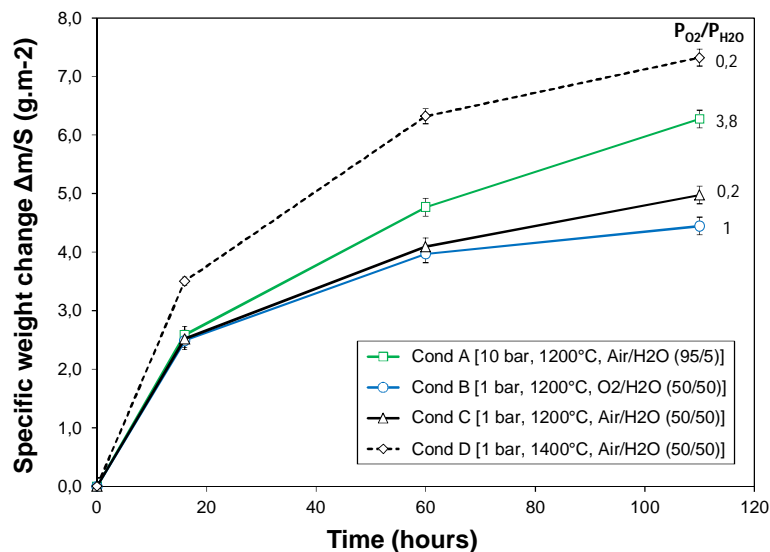


Fig. 2: Specific weight change as a function of time during steam exposure at high temperature (1200 and 1400°C) for CVI-SiC/SiC composite tubes.

For all the investigated conditions, the weight change corresponds to a relatively low gain (between 0.82 and 1.32%) indicating a limited corrosion effect after exposure during 110h at 1200 or 1400°C. As expected and evidenced by metallographic examinations of specimens showing the presence of silica on surface, this reflects a global behavior resulting from the simultaneous oxidation of the composites, mainly the matrix, to form a protective oxide layer and its volatilization. The various curve progressions demonstrate the rate dependence to the partial pressures of oxygen and water, and to the temperature.

- **Analytical approach and determination of the kinetic constants**

This mixed regime is partly explained by the higher solubility of water in the silica relative to oxygen. As a consequence, the oxidation rate (k_p) is affected by the volatilization rate (k_i) and the overall kinetics can be described in terms of measured weight changes by a parilinear kinetics as follows [11]:

$$t = \frac{\alpha^2 k_p}{2k_i^2} \left[-\frac{2k_i \frac{\Delta m_{ox}}{S}}{\alpha k_p} - \ln \left(1 - \frac{2k_i \frac{\Delta m_{ox}}{S}}{\alpha k_p} \right) \right] \quad \text{with} \quad \alpha = \frac{M_{SiO_2}}{M_{SiO_2} - M_{SiC}}$$

where t is the oxidation time (in hour), $\Delta m_{ox}/S$ is the surface weight gain due to growth of the silica scale and M_i is the molecular weight of the species shown in subscript.

The total observed weight change $\Delta m_{exp}/S$ is then given by the sum of the two contributions $\Delta m_{ox}/S$ and $\Delta m_{vol}/S$ that represents the surface weight loss due to oxide volatilization. After a relative long time when the limiting oxide scale thickness is achieved, the weight change can also simply be expressed by the following expression introducing a recession rate (k_r).

$$\frac{\Delta m_{vol}}{S} = -k_r t = -\frac{M_{SiC}}{M_{SiO_2}} k_i t$$

The oxidation constants were determined by interpolation from experimental silica thicknesses measured on specimen. For each conditions at 1200°C, a couple of rates (k_p, k_i) was identified and reported in Table 4, as well as the recession rate (k_r).

Table 4 – Identification of the parilinear rate constants for different conditions at 1200°C.

Conditions	Parilinear rate constants		
	k_p ($\mu\text{m}^2_{SiO_2} \cdot \text{cm}^{-4} \cdot \text{h}^{-1}$)	k_i ($\mu\text{m}_{SiO_2} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$)	k_r ($\mu\text{m}_{SiC} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$)
A [10 bar, 1200°C, Air/H ₂ O (95/5)]	0,178	$6 \cdot 10^{-7}$	$2,88 \cdot 10^{-7}$
B [1 bar, 1200°C, O ₂ /H ₂ O (50/50)]	0,171	$1,12 \cdot 10^{-2}$	$5,37 \cdot 10^{-3}$
C [1 bar, 1200°C, Air/H ₂ O (50/50)]	0,143	$1,12 \cdot 10^{-2}$	$5,37 \cdot 10^{-3}$

- **Residual mechanical tensile behavior**

Because both the integrity and the geometry of specimens were fully retained after oxidation, tensile tests up to failure may have been carried out to determine the residual mechanical behavior at room temperature. Results are presented in figure 3. To assess the influence of oxidation, the reference mechanical tensile behavior of an unexposed material without unloading-reloading cycles is reported. Table 5 summarizes the measured residual mechanical properties for each condition.

Table 5 – Residual mechanical properties at room temperature of specimens after oxidation.

Condition	Tensile test	E (GPa)	Strain to failure (%)	Tensile strength (MPa)
Unexposed ^(*)	Monotone	280 ± 10	0,66 ± 0,03	456 ± 18
A	Cycled	260	0,66	417
B	Cycled	259	0,63	413
C	Cycled	254	0,69	455
D	Cycled	256	0,65	390

(*) Three specimen tested

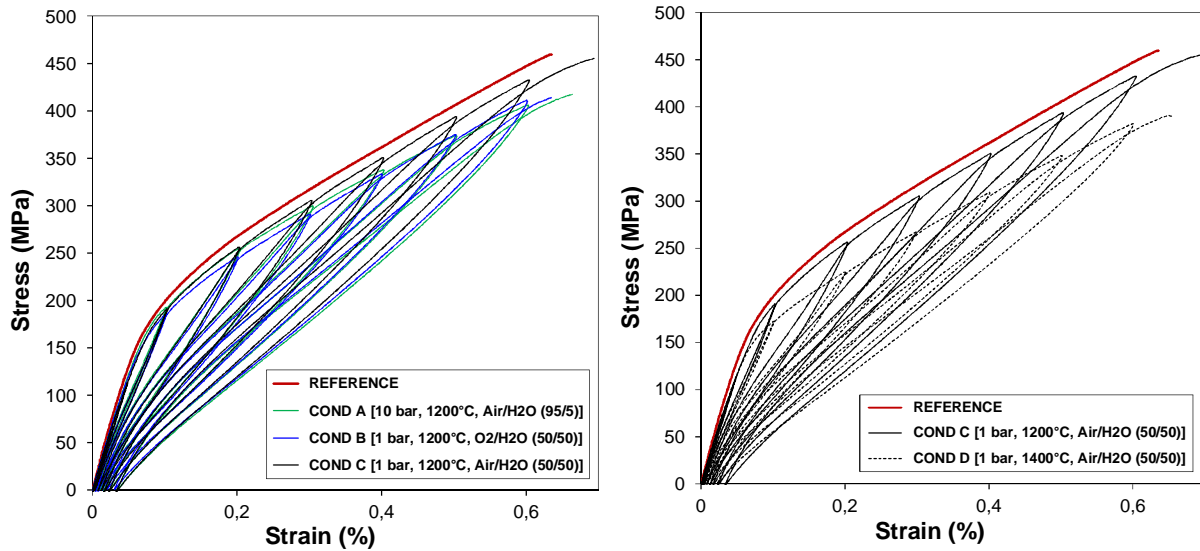


Fig. 3: Residual tensile stress-strain curves of specimens after oxidation, Comparison to the reference behavior without oxidation (monotonic).

Once again, specimens retain a similar “non-linear elastic damageable” mechanical behavior (without plateau) for all the investigated environments. This is a typical behavior for a CVI-SiC/SiC composite material with a pyrocarbon interphase that is characterized by a progressive damage, usually caused by matrix micro-cracking and interfacial debonding until failure. Specimen treated at 1200°C and 1400°C in the different steam environments lead to a very good retention of the strain to failure. A slight decrease of the tensile strength (lower than 10 and 15%) compared to the reference behavior of the non-oxidized material is observed. Moduli of elasticity (E) undergo a decrease of the same order.

The tightening of the hysteresis loops, as well as the low residual strain after unloading for specimen exposed at 1400°C would indicate a higher fiber-matrix load transfer due to oxidation, thus a strong interfacial shear stress.

• Discussion and mechanism

At 1200°C, the oxidation conditions investigated did not cause a significant reduction of the residual mechanical properties. All the tested specimens preserve a characteristic damageable mechanical behavior very close to the reference. The fracture surfaces are similar and exhibit wide non-brittle areas characterized by non-oxidized fiber pull out with lengths higher than a hundred micrometers. If no significant difference was observed at low magnification between fibers located at the heart or close to the edges of the composite, the polished cross-section observations at higher magnification reveal some oxidized areas on the surface but without degradation of the fiber reinforcements. This is attributed to the formation of silica from the consumption of the silicon carbide matrix, which ensures a protective function against oxidation. The presence of pyrocarbon at the fiber/matrix interfaces is evidenced using EDS facility.

At higher temperature (1400°C), the same investigations on post-mortem specimens reveal fractures surfaces with a slightly more degraded appearance. The presence of well-marked cracks, preferentially located near the matrix layer on the external surface (seal-coat) emphasizes a greater sensitivity to damage in this condition. This result is consistent with the weakening of the residual mechanical properties measured on specimens oxidized at 1400°C compared to the lower investigated temperatures. Here, the oxidation kinetics of the matrix seems to be sufficiently rapid to produce an efficient protective oxide layer but also causes local penetrations of oxide at surface cracks (whether these were pre-existing or appeared during thermal cycles). As a consequence, the presence of oxidized areas in contact with the fibers may be possible which would induce a mechanical anchorage that locally reinforces both the fiber-matrix bonding and the load transfer.

A schematic representation of the assumed oxidation process is depicted in Fig. 4.

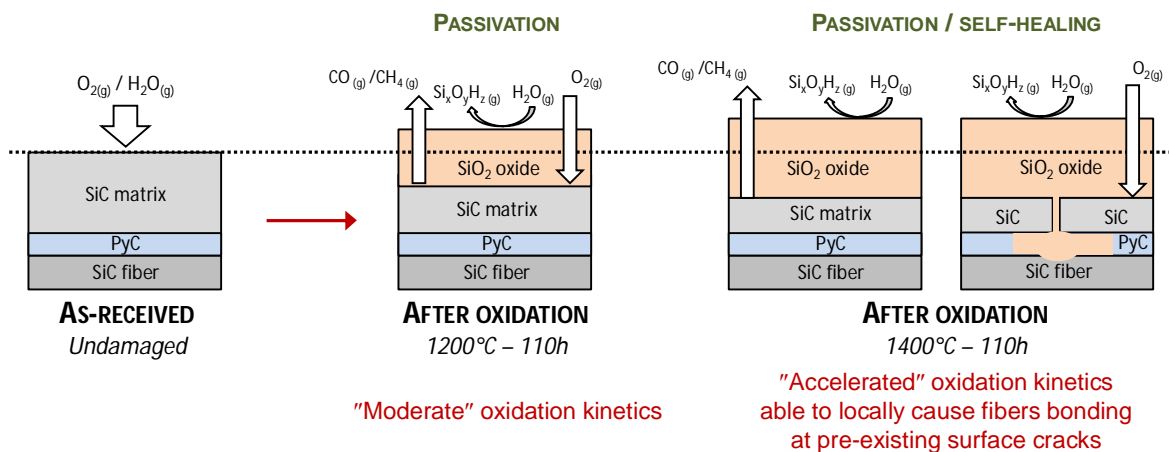


Fig. 4: Proposed oxidation process of CVI-SiC/SiC composite materials under high temperature steam environment.

Conclusion

First experiments were conducted on nuclear-grade tubular SiC/SiC composite produced at CEA to assess their ability to survive in representative LWR normal operating conditions. The key findings of this work highlight an excellent retention of the mechanical behavior after 5 months exposure to LWR water. In qualitative agreement with other recent studies, a material recession was observed but stays limited to a low weight loss in a closed system (autoclave).

In a second part, the low sensitivity of SiC/SiC composites under the high temperature steam conditions was confirmed. Once again, no significant degradation of the mechanical properties of CVI-HNI SiC/SiC specimen is observed after relatively long exposure times (beyond 100 h at 1200°C).

These preliminary results are positive but significant studies and developments are still necessary to close the technology gap. Qualification for nuclear application requires substantial irradiation testing, additional characterization and the definition of design rules applicable to such an innovative material. Consequently, the use of a SiC-based fuel cladding shows promise for the highest temperature accident conditions but remains a long term perspective.

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