QUENCH BEHAVIOR OF SiC/SiC CLADDING AFTER A HIGH TEMPERATURE RAMP UNDER STEAM CONDITIONS

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ABSTRACT: *The present work reports the results from experiments on SiC/SiC clad segments demonstrating their outstanding ability to preserve a coolable geometry during the reflood phase of a postulated design basis Loss Of Coolant Accident (LOCA) and beyond. Experimental assessments of thermal shock performance were investigated for this purpose by quenching specimens from 1400°C and 1500°C under steam environment into room temperature water. SiC/SiC composites remain structurally sound and retain their mechanical properties. Post-quenched SiC/SiC tubes were subjected to internal helium gas pressure to test the permeation of the structures. These tests established the link between the leak-tightness measurements and damages in the microstructure through micro crack initiation. Close examinations of the oxidized surfaces evidence the efficiency of the passivation layer in protecting substrates. Finally, a correlation of the observations with the oxide growth rate is developed to support a better understanding of the mechanisms as well as the prediction of the acceptable limits of application. These positive results reinforce the interest of a SiC-based fuel cladding concept to enhance the accident tolerance of fuel for future reactors.*

KEYWORDS: *Silicon carbide, SiC/SiC composite, Accident Tolerant Fuel, quench, oxidation.*

I. INTRODUCTION, MATERIALS AND EXPERIMENTAL DETAILS

Silicon carbide based continuous fiber ceramic matrix composite materials (SiC_f/SiC) are considered by the French Nuclear Institute as a long-term option for Gen III/III+ light water reactor (LWR) cladding to improve the accident tolerance of the fuel (ATF) [1,2]. Consistent with this ambition, the extensive R&D activities over the post-Fukushima period has resulted in significant progress in the fabrication of representative and functional specimen, removing some of the technological barriers that prevent such advanced ceramic materials from use in a nuclear environment. In addition to on-going basic research, a collaborative program was launched to assess the thermo-mechanical performances of SiC/SiC composites produced at CEA and to collect the required data for a preliminary conceptual design.

Among the acceptance criteria, it is an essential prerequisite for emerging fuel claddings to maintain a coolable geometry during the re-flooding phase of a Loss of Coolant Accident (LOCA) that induces tremendous thermal stresses, as the temperature rapidly drops over a short period. Because the cladding acts as the first containment barrier, retention of the fission products as well as resistance to fragmentation are also considered highly desirable in a LOCA event [3,4]. For this reason, the SiC/SiC composites, characterized by a higher fracture toughness than the SiC monolithic ceramics, are preferred since they offer the ability to accommodate mechanical stresses by matrix micro-cracks development with crack arrest capabilities. The drawback of the composite toughening mechanism is the loss of impermeability that encouraged the development of a multilayered cladding design including the presence of a metal liner [5]. The presumably fair ductility of the metal ensures it to withstand any strain imposed by the deformation of the composite, so that the leak-tightness is guaranteed until the ultimate failure of the composite occurs, thus considerably extending the leak-tight domain.

On the other hand, a multilayered cladding design does not argue in favor of an optimal radial heat transfer through the cladding wall thickness due the interfacial thermal resistances [6,7]. This could be exacerbated by inherent porosity of the SiC/SiC composites [8] and it should be carefully analyzed to which extent the SiC/SiC composites could endure significant stresses in case of re-flooding phase of a postulated LOCA event and beyond. The present work reports preliminary results of the assessments of the thermal shock resistance and quench survivability on nuclear grade SiC/SiC composites, considered as elementary constituent layers.

I.A. CVI-SiC/SiC composite tubes

Specimens evaluated in this study were tubular SiC/SiC composite segments of 60 mm lengths with representative LWR cladding diameters. The fibrous architecture consists of a combination of filament winding and 2D braiding layers produced with an angle of ± 45° from Hi-Nicalon Type S reinforcements. They were chemically vapor-infiltrated on CEA facilities with a pyrocarbon (PyC) interphase thickness of less than 100 nm to provide adequate fiber-matrix load transfer. Efforts have been made to reduce the porosity to a minimal level; the apparent density is about 2.85 to 2.90 with a fiber volume fraction of 35%. Inner and external surfaces were carefully smoothed by fine grinding.

I.B. Oxidation experiences

Specimens were subjected to high temperature oxidation under steam followed by quenching. The heating phase took place under inert helium atmosphere up to 1100°C with a rate of 1°C/s. Once 1100°C was reached, a 100% steam flow rate was injected inside the vertical alumina chamber while maintaining continuous heating up to the target test temperature. After a minimal period of exposure depending on the investigated conditions, suspended specimens were quickly dropped into a room temperature water pool by means of an electrically driven pin.

Fig. 1 shows two typical temperature profiles applied to SiC/SiC composites with a steam holding time of 100s at respectively 1400 and 1500°C.

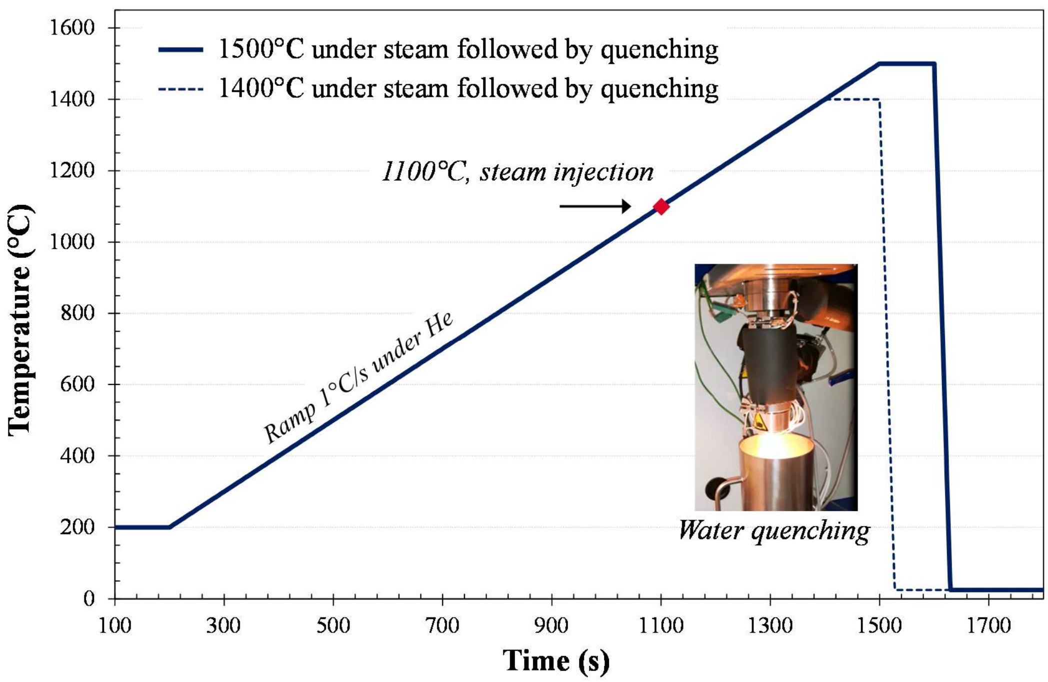

Fig. 1. Typical test sample heating profiles at both 1400°C and 1500°C.

II. RESULTS AND DISCUSSIONS

II.A. Subcooling effects after a high temperature ramp followed by quenching

All tested specimens survived the oxidation experiments with a fully preserved integrity and geometry after the thermal shocks. Over the temperature range of 1400 to 1500°C, no weight change can be accurately measured for lower exposure times. Consistent with the paralinear oxidation kinetic of silicon carbide under high temperature steam conditions [9-11], a minimum of 1 hour is required to expect a significant change of weight.

Post-test examination by means of scanning electron microscopy (SEM) evidenced the presence of matrix micro-cracking, preferentially located near the surfaces as it can be seen in Fig. 2. The density of cracks is very low and does not appear to be related to the exposure time since visual examinations exhibited similar observations regardless the specimens. No crack propagation was commonly observed for all the tested SiC/SiC tubes. Single micro-crack initiation occurs primarily at the inside surface of the composite while initiation occurring from the outside surface of the specimen being rare. It can be assumed that thermal stresses faced during quenching generated cracks along the inside surface of the sample where the stress concentration is higher due to the curvature. The presence of pre-existing pores on crack development/propagation does not have any influence. Note that none of the high temperature exposures followed by quenching seem to affect the critical fiber-matrix interphase since the damage remains limited near the specimen surfaces. Such a result contrasts with brittle monolithic silicon carbides that immediately shatter into multiple pieces upon water quenching [12].

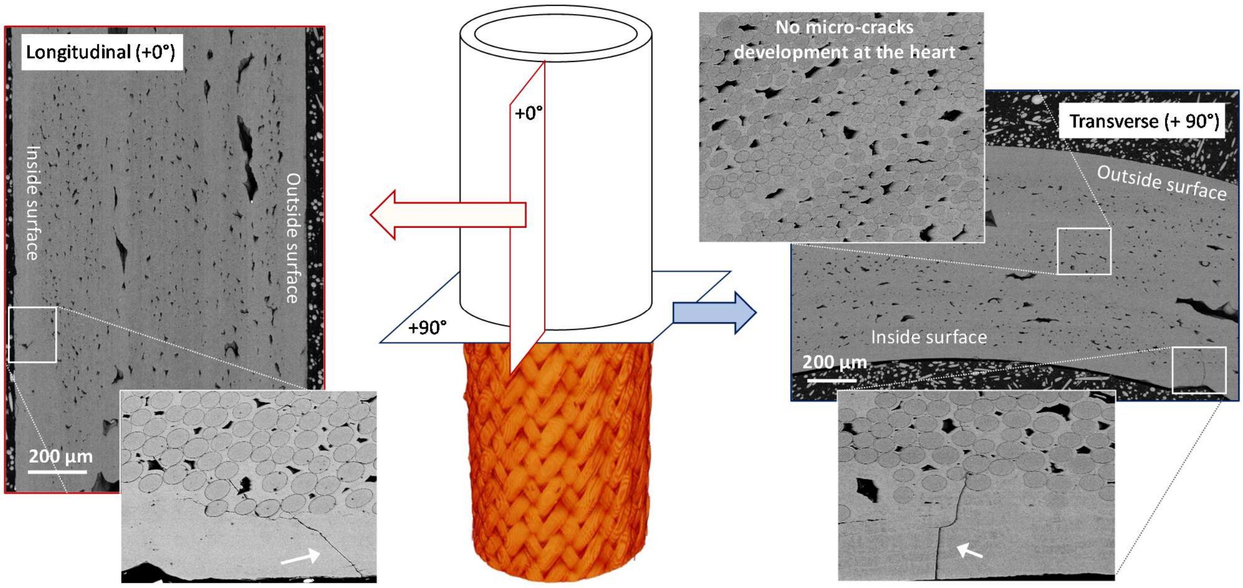

Fig. 2. SEM microstructural examinations (longitudinal and transverse sections) of a characteristic SiC/SiC tube oxidized at 1500°C under steam during 100s before being quenched in water at 25°C.

Obviously, the thermal conductivity plays a key role in removing excessive thermal stresses induced by rapid cooling but the heat transfer coefficient of liquid-solid contact should also have a significant influence. In similar experiments, the nucleate boiling process, that strongly depends on the material surface characteristics, is put forward to justify a microstructure preservation from damage after thermal shock [13].The short period of nucleation boiling leading to bubble generation would contribute to reduce the thermal gradient and therefore minimize the thermal stress within the SiC/SiC specimen thickness. Since the surface temperature of sample was significantly reduced during this phase, the developing thermal stresses do not reach the critical level that would damage the ceramic structure. As discussed in [14,15], quenching in a boiling water bath would be considered more beneficial yet from that point of view because of the absence of a transient period.

Despite a limited damage on the surface regions, the extent of matrix micro-cracking caused by quenching is expected sufficient to generate interconnected pathways throughout the bulk of the composite. Through helium gas leak tightness measurements under internal pressure, a comprehensive evaluation allows to establish a close relationship between the leak rate data and the contributing factors on quenched specimen. The quenching temperature, as well as the inherent characteristics of the material like porosity and surface finish are demonstrated to have some incidence on the results.

It may further be noted that the formation of a dense and homogeneous silica scale was detected on the surface of specimen after quenching. However, no trace of local oxide penetration into the composites substrates was observed. X-ray photoelectron spectroscopy (XPS) analyses make it possible to estimate thicknesses of an order of several hundred nanometers (300 nm after 1500°C exposure for 100s). The temperature/oxidation time couples explored in this paper do not involve the surface bubble formation as reported elsewhere [16].

II.B. Mechanical behavior after quenching

Thermal shocked specimens were tested up to failure in tensile loading after quenching to investigate the residual mechanical performances (in accordance with ISO 20323 [17]). As shown in Fig. 3, the damage induced by the thermal shock did not significantly impact the mechanical behavior which exhibits a typical "non-linear elastic damageable" curve of CVI-SiC/SiC tubes. Young modulus (EP), yield strength (σ_Y) and strain at ultimate failure (ε_m) remain unchanged in comparison to the composite reference properties (see Table 1). Better yet, quenched tubes tended to induce higher tensile strength which could result from an increase of the matrix strength. Such an observation suggests a surface crack healing related to silica formation under steam. Similar effects could also be induced by a reduction of the Weibull's modulus characterized by a scatter in strength data. Thus, the matrix cracks would be formed at increasing stress levels as reflected by the measured non-linear domain of deformation. An associated mechanical behavior was already modeled on SiC/SiC minicomposites by Lissart et al [18]. Whether the specimens were quenched or not, only a single regime of acoustic emission was detected indicating that matrix cracking saturation did not occur up to the ultimate failure.

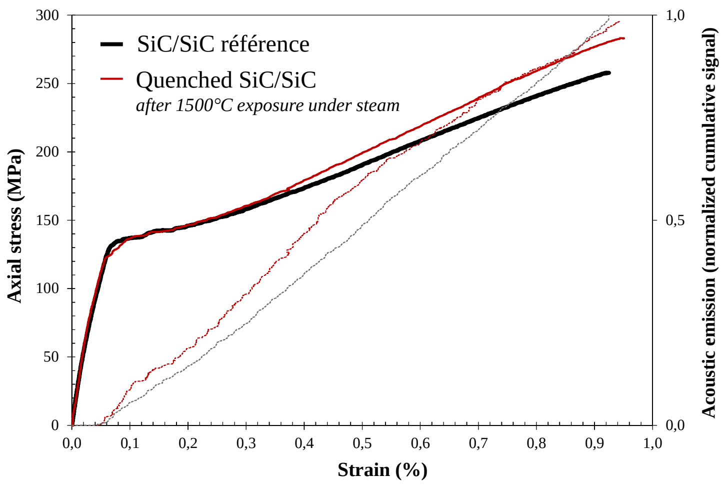

Fig. 3. Tensile stress-strain mechanical behavior of quenched SiC/SiC tube after 1500°C exposure under steam for 100s. Also given for comparison is the reference stress-strain curve measured on as-fabricated SiC/SiC tube.

Table1. Features of the stress-strain behavior measured in tensile on reference and quenched SiC/SiC composites.

	Young modulus *EP (GPa)*	Yield strength σ_Y (MPa)	Tensile strength σ_m (MPa)	Strain at ultimate failure ε_m (%)
SiC/SiC Reference *(averaged over 3 tubes)*	285 ± 3	97 ± 6	252 ± 8	0.95 ± 0.03
Quenched SiC/SiC after 1500°C exposure under steam	280	104	283	0.95

III. CONCLUSIONS

Quench behaviors of SiC-based composites after high temperature steam oxidation were investigated as part of the feasibility assessment for LWR fuel cladding application. Thermal shock experiments performed from 1500°C to room temperature water demonstrate outstanding ability for SiC/SiC clad segments to preserve a coolable geometry during the re-flooding phase of a postulated design basis LOCA event. Results showed a high strength resistance with maintenance of the capabilities for the composite to accommodate thermal stress by matrix micro-cracking. The micro-cracking was nevertheless very limited which suggests that SiC/SiC composite cladding would survive a quench in a LOCA scenario while limiting the release of radioactive material from the fuel rod. Consequently, using SiC/SiC cladding was lead to significant gains in an accident scenario. These positive results reinforce the interest of a SiC-based fuel cladding concept to enhance the accident tolerance of fuel for current and future reactors.

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