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INVESTIGATION OF TAILORED SIC/SIC COMPOSITES FOR SODIUM-COOLED FAST REACTORS

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Increasing the sustainability and the safety of nuclear reactors require the development of new types of reactors (GEN-IV systems) which can work as breeder (producing more fuel that it consumes) and can offer the possibility of burning minor actinides to reduce the waste, such as the Sodium- (SFR) or the Gas-cooled (GFR) Fast Reactors. Therefore, there is a need to assess materials which can withstand these very harsh core conditions. In this aim, SiC/SiC composites are promising candidates thanks to their high decomposition temperature (> 2000°C), low swelling and creep under irradiation and good neutron transparency. A recent CEA patent has highlighted that SiC/SiC-based hexagonal tubes would increase the resistance to melting and, as a consequence, the safety of the SFR core. In this way, techniques have been developed to manufacture a SiC/SiC hexagonal tube with given dimensions, which has a relatively low level of porosities and a pseudo-ductile mechanical behavior (tolerance to deformation). Besides, the chemical compatibility between SiC and SiC/SiC composites towards liquid sodium and its impurities (in particular oxygen) was investigated. For this purpose, two sets of experiments were conducted in the CORRONa² facility (CEA). On the one hand, immersions up to 2000h in an oxygen-purified ([O]<10ppm) liquid sodium heated up to the nominal temperature of a SFR (550°C) were carried out. On the other hand, oxygen was inserted in the liquid sodium to reach important oxygen quantities ([O] = 1000 ppm), well above the reference considered for incidental and transient states, to investigate the influence of this element on the SiC/SiC composites. Indeed, the SiC/SiC composites and their pyrocarbon interphase (employed to have a good linkage between the fiber and the matrix) can encounter active or passive oxidation at high temperatures. Mass assessments, SEM, XPS, X-ray tomography and tensile tests were conducted to characterize the sample properties before and after immersion. As a result, it was observed that there is no significant degradation of the material after exposure to either the oxygen–poor or –rich environments. Moreover, in some cases, an increase of the mechanical properties of SiC/SiC composites was observed.

I. INTRODUCTION

Among the materials under investigation for nuclear applications, Ceramic Matrix Composites (CMCs) have aroused many interest to increase both the performance and the safety of either the fusion or the fission nuclear reactors. Especially, silicon carbide reinforced silicon carbide composites (SiC/SiC) are promising candidates for cladding and structural applications because of their mechanical resistance at high temperature, their chemical inertness and their stability under irradiation. Regarding the cladding, they constitute the main solution for the high temperature core of the gas-cooled fast reactors (GFR) in nominal (≈ 1000°C) and accidental conditions (up to 2000°C). Recently, SiC/SiC composites have gained interest for light water reactors (LWR) in the framework of the accident tolerant fuels to avoid the oxidation issue inherent to the use of a zirconium-based cladding during accidental conditions (Ref. 1). Multiple issues are still at stake for cladding applications such as the evolution of the thermal conductivity of SiC/SiC under irradiation and the chemical compatibility with the fuel. On the contrary, some structural applications do not need those requirements. A recent CEA patent has highlighted the potential benefits of a SiC/SiC hexagonal tube for sodium-cooled fast reactors (SFR), which provides the structural integrity of the fuel assembly and guides the liquid sodium flux (Fig. 1) (Ref. 2). In this concept, swelling under irradiation and creep at high temperature currently encountered respectively by austenitic or ferritic/martensitic steels will be limited, even avoided. This CMC assembly has to meet the conditions of the SFR reactors. Therefore, it has to be chemically compatible with sodium up to its boiling point (883°C) and the assembly body alloys and a limited swelling in the operating condition (≈ 550°C) under high irradiation doses (more than 100 dpa at the end of life). Due to the lack of extensive studies (Ref. 3, 4), the chemical compatibility of CVD SiC and SiC/SiC composites towards liquid sodium in the nominal operating temperature (550°C, 1 bar) up to 2000 h was investigated. Moreover, the effect of the sodium immersion on the

mechanical behavior of tubular SiC/SiC composites was assessed for undamaged and predamaged samples prior to exposure. Tubular geometry was retained from the feedback obtained on the cladding materials studies.

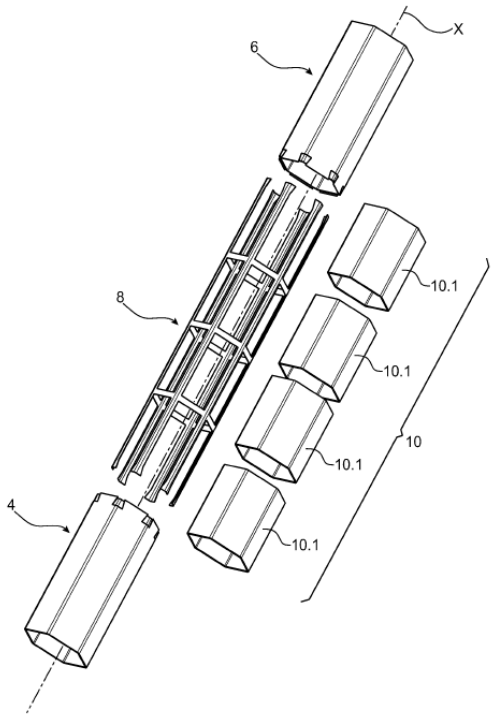

Fig. 1. Hexagonal tube composite assembly body for SFR (Ref. 2)

II. MATERIALS AND METHOD

I.A. Samples

Silicon carbide Hi-Nicalon S fibers were selected as the composite reinforcement. They were shaped in a tubular geometry through 1 layer of filament winding and 2 layers of 2D braiding at 45° to achieve a good mechanical behavior under tensile or internal pressure stresses. Prior to the deposition of the SiC matrix by chemical vapor infiltration, a thin (< 50 nm) pyrocarbon layer is deposited. The latter will ensure the pseudo-ductile mechanical behavior expected for the SiC/SiC composites. After the matrix consolidation and densification, the composites have a residual porosity of 5 to 10 %. They are grinded on surface to have a regular cross section along the tube as well as a smooth surface to reach respectively a final internal diameter, external diameter and a length of 7.81, 9.55 and about 70 mm. The CVI technique was chosen because it leads to very high purity materials (Ref. 5), comparable to the composition of the CVD SiC purchased from Technical Glass Company.

II. B. Mechanical set-up

The mechanical behavior of the SiC/SiC composites was evaluated thanks to cycled uniaxial tensile tests on 65 to 70 mm length composites. A structural epoxide resin (3M Scotch-Weld$_{TM}$ 9323 B/A) was used to fix the tubes in the extension system (Ref. 6) which is fixed on an INSTRON 2404 mechanical testing machine. The upper part is mounted on a HBM U10M force sensor (max. 25kN). The longitudinal and diametric strains were measured with respectively a 25 mm gauge INSTRON 2620-603 and a MTS 632.19F-20 extensometers that were calibrated with a high resolution numerical calibrator. An acoustic emission sensor was systematically used to precise the damaging thresholds and to highlight the microstructural couplings. It was fixed on the force sensor. The results are gathered as a cumulated signal. Only the signals over 50 dB (corresponding to the background plus 10 dB) are taking into account. 7 cycles of loading/unloading were realized during the cycled tensile tests from 0.05% to 0.5% longitudinal strains to generate samples predamaged at different levels prior to immersion.

II.B. Experiment procedure

The sodium (2 kg) was introduced in a closed molybdenum lined crucible. The setup and the preparatory steps of the sodium bath were already described elsewhere (Ref. 7). The sodium bath was purified by zirconium foils to reduce as much as possible the oxygen concentration prior to the testing (Ref. 8). Two oxygen concentrations of the sodium bath were chosen. On the one hand, a zirconium foil is introduced along with the samples in the oxygen purified experiment to maintain the oxygen concentration as low as possible during the immersion of the samples. On the other hand, an Alfa Aesar Na_2O/Na_2O_2 powder is introduce along with the samples in the oxygen-rich set of experiments to reach a final oxygen concentration of 1000 ppm, which is under the solubility limit at 550°C (1936 ppm) (Ref. 9). The samples are inserted in the liquid sodium environments at 110°C. This temperature was selected for the relatively low vapor pressures of sodium. The samples are heated up to 550°C though a temperature ramp of 4°C/min for 1000 h. After a cooling to 215°C, some of the samples are pulled out for analysis while the remaining ones are immersed for a total of 2000 h (Fig. 2).

II.C. Sample Analysis

The samples are cleaned 3 times in acetone before their immersion in the liquid sodium. There are cleaned several times after the immersion with ethanol then water to neutralize the remaining sodium and weighted to evaluate the mass evolution. XPS analysis (Thermo

Scientific Escalab 250 xi spectrometer) was also used to determine the surface composition of the samples. The same mechanical testing arrangement was also used to determine afterwards both the undamaged and predamaged prior to immersion the SiC/SiC composites mechanical behavior.

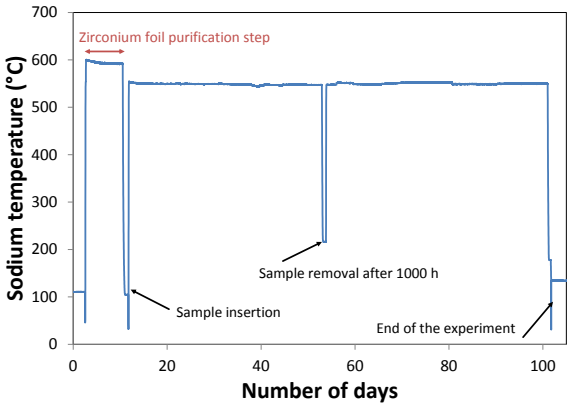

Fig. 2. Settings of the experiments as a function of time.

III. RESULTS

All the samples were weighted after cleaning. Different behaviors of the CVD SiC were observed as a function of the sodium oxygen content with resp. no weight loss and a slight weight diminution (- 0.63 %) in the oxygen-purified and oxygen-rich environments. SiC/SiC composites exhibit a small weight gain after immersion (< + 1 %). This result was attributed to the porosity levels (5 – 10 %) of the SiC/SiC composites. Indeed, X-ray tomography highlights the presence of remaining sodium or sodium containing components (NaOH, Na_2O, Na_2CO_3) in the sample. This phenomenon may be attributed to the porosities opening at high temperatures due to thermal volume expansion, which are closed during the cooling down of the samples. Moreover, it was observed during the storage of the SiC/SiC composites the generation of sodium oxides on the samples surface. Also, no influence of either, the composites level of predamaging, or the experiment duration, were highlighted.

Different surface oxygen concentrations were detected by XPS analyses (Tab. 1) as a function of the sodium bath experiment oxygen content. Indeed, after the oxygen-purified sodium exposure, the CVD SiC surface encounters reduction with an increase in the SiC fraction (91 % at. instead of 82.1 % at. for the reference sample). On the contrary, an oxidation of the surface is observed after immersion in the oxygen-rich environment (54.4 % at. of SiC). The composition of the composites surface could not be determined because of their roughness.

TABLE I. Composition of the CVD SiC surface

Fraction (% at.)	Without sodium exposure	After 2000 h in the O-purified	After 2000 h in the O-rich
SiC	82.1	91.0	54.4
SiO_xC_y	12.8	7.5	29.7
SiO_2	5.1	1.5	15.9

The stress/strain curves after 1000 h and 2000 h immersion in the sodium environments are plotted on Fig. 3. An increase in the failure strains and stresses (Tab. 2) (resp. up to 24% and 32%) along with the increase of the stress for a given strain were observed. No clear influences of neither the immersion duration, nor the oxygen content were observed. Also, a slight increase of the Young's moduli was noted. It was observed that the main differences in the mechanical behaviors occur during the low level deformation (< 0.05 % of longitudinal strain) (Fig. 4). Indeed, for the reference samples, differences between the beginning of the acoustic emission, characteristic of the matrix multicracking, and the end of the linear domain occurred, while they should have come at the same time. Nonetheless, after the immersion tests, this phenomenon was not detected.

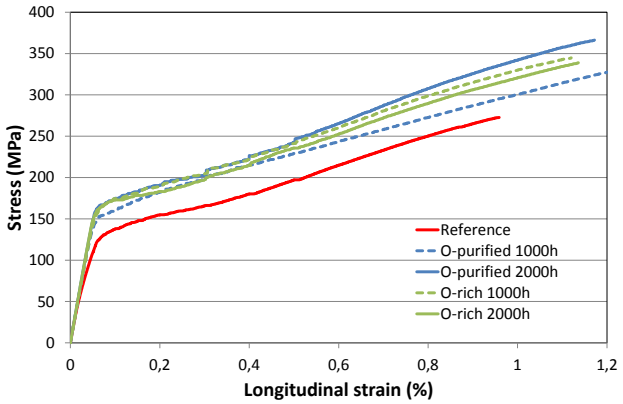

Fig. 3. Envelop of the stress/strain curves for the reference and after immersion in the oxygen-purified and -rich environments SiC/SiC composites samples.

TABLE II. Failure longitudinal strains (ε) and stresses (σ) and Young's modulus (E_0) for the reference sample and after sodium immersion.

Sample	ε (%)	σ (MPa)	E_0 (GPa)
Reference	0.959	273	293
O-purified 1000h	1.200	328	308
O-purified 2000h	1.172	366	310
O-rich 1000h	1.120	345	297
O-rich 2000h	1.136	339	310

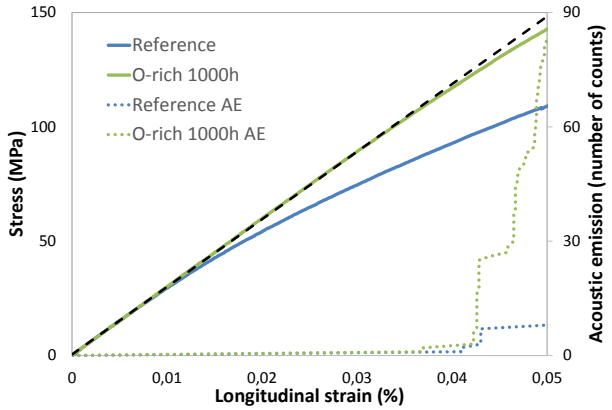

Fig. 4. Deviation from linearity and beginning of the acoustic emission of the reference and after sodium immersion (O-rich 1000h) samples.

No evolution of the area and the full width at half maximum of the cycles was observed. However, the residual strains (after the stress release) increase drastically after immersion by a factor 4 for both conditions.

As far as the predamaged to immersion samples are concerned, two distinct mechanical behaviors are highlighted. The investigations have been focused on the samples that encountered the oxygen-purified environment (Fig. 5.). One the one hand, for the tubes predamaged at 0.05 % prior to immersion, the same behavior as the undamaged samples after sodium exposure is observed. On the other hand, samples predamaged over 0.1% exhibit the same strains and stresses at failure along with the same behavior as the reference materials.

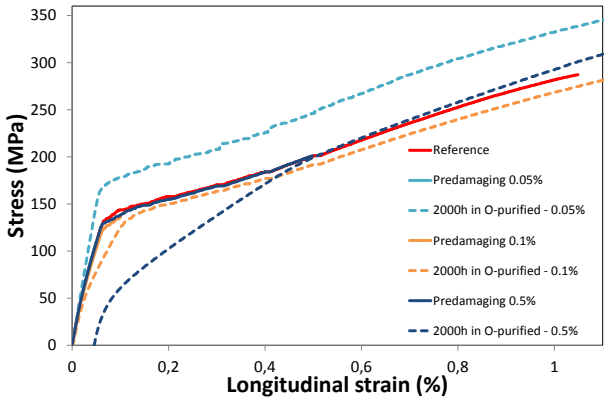

Fig. 5. Stress/strain envelops of the reference and predamaged samples (without sodium immersion) and of the predamaged samples afterwards the immersion for 2000 h in the oxygen-purified environment.

IV. DISCUSSION

Considering the slight weight changes of the CVD SiC samples, it can be concluded that the reduction and oxidation in respectively the oxygen-purified and oxygen-rich environments are limited. The low weight gain of the SiC/SiC composites is attributed to the trapping of sodium following the thermal expansion of the material at the immersion temperature (550°C). This is demonstrated by the release of sodium components on the composite surface after cleaning and the X-ray tomography analysis. Also, the increase of the residual strains after unloading for samples immerged in both sodium environments can be attributed to the sodium trapping. Therefore, during the loading, the porosities are opened and the trapped sodium can then react with either the dioxygen, the carbon dioxide or the water of the ambient atmosphere. The formed components can then block the composites microcraks closure, leading to an increase in the residual strains after unloading.

The absence of diminution of the failure strains and stresses after immersion shows that sodium has no negative influence on the composites mechanical properties. Moreover, the pyrocarbon interphase of the SiC/SiC composites appears to be neither modified nor degraded after its exposure to the liquid sodium, regardless of the oxygen concentration. Indeed, the predamaged samples, the interphase of which was exposed to sodium environments because of the generation of microcracks, do not exhibit any degradation of their mechanical properties.

Besides, the increase of the failure strains and stresses for the samples undamaged and for some predamaged at 0.05 % before sodium exposure (which has not exhibited any acoustic emission) shows that the origin of this phenomenon might occur during the fabrication of the composites. Indeed, the stress gap for a given strain appears for low strains and seems to be constant after the beginning of the matrix multicracking. Tests on SiC/SiC plates will determine if there is any influence of the fabrication process on the mechanical behavior of the SiC/SiC composites after sodium exposure.

The low variation of the Young's modulus of the SiC/SiC composites shows that no influence on either the fibers or matrix has occurred. This slight increase can be attributed to the presence of sodium in the composite porosities, following the law of mixtures of the Young's modulus.

From an application point of view, these results are encouraging for SiC/SiC composites that will stay for years in the core of the reactor. However, to conclude on this aspect, long duration but especially loop experiments

are still needed. Indeed, the thermal gradients in a sodium loop (inherent of the presence of a heat exchanger system) can generate differential corrosion with respectively the dissolution and deposition of C and/or Si on the hot and cold spots of the circuit.

V. CONCLUSIONS

Following the increase in the safety and the efficiency of nuclear reactors, SiC/SiC composites are currently considered as core materials but its use still needs several investigations. However, for structural applications, such as the hexagonal tubes of the SFR, fewer issues are at stake. In this aim, the chemical compatibility between CVD SiC and SiC/SiC composites towards sodium environments was studied. Moreover, the mechanical behavior of SiC/SiC composites was assessed after sodium exposure. Two conditions were selected for this study to dissociate the effect of the sodium and its impurities, especially oxygen (oxygen-rich and oxygen-purified environments). It was observed that the CVD SiC shows only a limited reaction towards sodium with a low weight loss after 2000 h in an oxygen-rich (1000 ppm) environment, well above the oxygen concentration considered for transient and accidental states. The SiC/SiC composites exhibit no degradation of their mechanical behavior after immersion in both environments, even if the pyrocarbon interphase was exposed. On the contrary, an increase of the mechanical properties of the undamaged samples after immersion was highlighted. This phenomenon was attributed to the fabrication method of the tubular SiC/SiC composites. Tests on SiC/SiC plates would confirm those results. The outcome of this study is encouraging for the use of SiC/SiC composites in SFR. However, more investigations are still needed, especially on the influence of the thermal gradients in a sodium loop on the chemical compatibility and the mechanical behavior of the SiC/SiC after sodium immersion.

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