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High-temperature tests of silicon carbide composite cladding under GFR conditions

Valentina Angelici Avincola^{a*}, Kerr Fitzgerald^b, Daniel Shepherd^b, Didem Kinay^a, Cédric Sauder^c, Martin Steinbrueck^a

^a Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

^b National Nuclear Laboratory, Havelock Rd, Derwent Howe, Workington, United Kingdom ^c DEN-Service de Recherches Métallurgiques Appliquées, CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

Abstract

This paper presents the results of tests performed on selected cladding materials in a well-defined atmosphere that reproduces the environment expected in a gas-fast nuclear reactor. In particular, the feasibility of silicon carbide composites is investigated in helium with impurities by means of a thermogravimetric device. The temperatures of the tests are in the range of normal operation conditions (900-1000 °C) and accident conditions (up to 1500 °C) of a gas fast reactor. Post-test analyses are carried out with scanning electron microscope. This work reports the transition temperature between passive and active oxidation of silicon carbide in helium and impurities atmosphere. Kinetics constants are provided for the linear weight loss.

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Keywords: Silicon carbide composites; oxidation; gas fast reactors; kinetics;

1. Introduction

Silicon carbide is studied as materials for nuclear applications since the development of the tri-layered isotropic micro-encapsulated fuels (TRISO) in the 1960s. The interest in SiC is due to its outstanding performance demonstrated under a wide variety of conditions, such as creep and oxidation resistance [1, 2, 3] and radiation tolerance [4]. Silicon carbide is nowadays under investigation as cladding with enhanced accident tolerance for light water reactors [5, 6], as well as cladding for Gen IV nuclear plants [7, 8].

Nomenclature

AFM	Atomic force microscope
CEA	French Alternative Energies and Atomic Energy Commission
CVD	Chemical vapour deposition
CVI	Chemical vapour infiltration
EDS	Energy-dispersive X-ray spectroscopy
GFR	Gas fast reactor
LFR	Lead-cooled fast reactor
KIT	Karlsruhe Institute of Technology
KI	Linear constant ($\text{mg}/\text{cm}^2\text{h}$)
NNL	Nuclear National Laboratory
ORNL	Oak Ridge National Laboratories
PVD	Physical vapour deposition
Ra	External roughness
SFR	Sodium-cooled gas reactor
SEM	Scanning electron microscope
TGA	Thermal gravimetric analysis
Tp-a	Temperature transition between passive and active oxidation
TRISO	tri-layered isotropic micro-encapsulated fuels
XPS	X-ray photoelectron spectroscopy

In the framework of the European Energy Research Alliance, a 4-years project called MatISSE (Materials' innovations for a safe and sustainable nuclear in Europe) has been launched in 2013 to investigate the performance and feasibility of materials related to advanced nuclear systems, such as lead-cooled fast reactor (LFR), gas fast reactors (GFR) and sodium-cooled gas reactors (SFR).

For these applications, the tri-layered “sandwich” design, which consists of two SiC matrix and SiC fibers (SiC/SiC_f) layers and an intermediate metal liner [9][10], is under investigation as fuel cladding. The combination of SiC fibers and matrix is particularly indicated since it provides pseudo-ductility to the SiC cladding [11], while the metal liner (tantalum in this case) helps maintaining the impermeability of the cladding for fission gas retention. Karlsruhe Institute of Technology (KIT), along with other European Institutions (e.g., the French Alternative Energies and Atomic Energy Commission (CEA), National Nuclear Laboratory (NNL)) are working together to test SiC/SiC_f prototypical materials in well-defined GFR conditions. In this paper, preliminary results of SiC/SiC_f specimens tested at high temperatures in a gas mixture that reproduces the GFR conditions are presented.

2. Experimental procedure

2.1. Samples

Tri-layered cladding samples were provided by CEA along with the two components, SiC/SiC_f , and tantalum tubes. In Figure 1 the SiC/SiC_f are presented: they consist of tube segments of a length of 10 mm, an external diameter of ≈ 10 mm and a wall thickness of ≈ 0.89 mm.

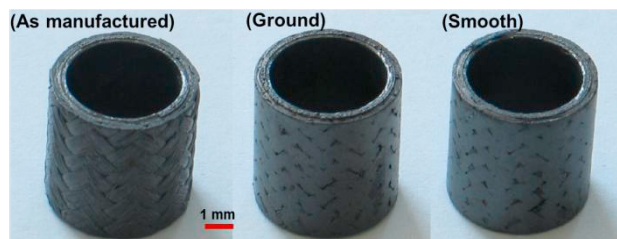


Figure 1. Macrograph of the SiC/SiC_f samples

Samples with three different external surfaces were tested in this work. The first is as manufactured, with an external roughness of $R_a \approx 50\mu\text{m}$. The second is called ground, since the external surfaces were subjected to mechanical grinding and over-coated with $\beta\text{-SiC}$ by physical vapor deposition (PVD) ($R_a \approx 10\mu\text{m}$). The third is called smooth, since it refers to the “ground” samples that have been subjected to an additional mechanical grinding ($R_a \approx 2\mu\text{m}$). In this work, the results obtained with the SiC/SiC_f layer without the Ta interphase are presented (Table 1).

Table 1 Samples tested in this work

T (°C)	Samples tested		
	<i>As manufactured</i>	<i>Ground</i>	<i>Smooth</i>
900	L1-11, L1-2	L2-1, L2-2	L3-1, L3-2
1200	L1-5, L1-6	L2-3, L2-4	L3-3, L3-4
1300		L2-5, L2-6	L3-5, L3-6
1400	L1-8	L2-8	L3-8
1500	L1-9	L2-9	L3-9

Each sample was cleaned before the test using DI water, isopropanol, and acetone, and then it was weighted with a benchtop balance and inserted into a thermogravimetric device.

The prescribed temperature for the tests was reached after a 30 °C /min heating phase in pure helium. The isothermal temperature was maintained for different times, with a maximum of 22 hours. The performance of this sample design was tested in this paper under normal operation conditions for GFR (900 °C), as well as under off-normal conditions according to the Oak Ridge National Laboratory (1200 °C, 1300 °C, 1400 °C and 1500 °C) [12].

2.2 Facility and post-test analyses

Tests presented in this work were performed in a thermogravimetric device (SETARAM TAG 24 16) able to reach temperature as high as 1700 °C. In order to understand the corrosion and erosion/corrosion behavior of SiC/SiC_f in a GFR environment, it will be important to understand the likely coolant chemistry. However, since no GFR has ever been built, no data exists on the chemistry resulting from an actual GFR helium purification system. Therefore, the GFR coolant chemistry used in the experiments considers the reported experience of the modern helium purification system of the currently operating Chinese HTR-10 prototype high temperature reactor (HTR) which is of similar scale to the proposed ALLEGRO GFR demonstrator [13]. It has been decided to focus on ALLEGRO as it is a nearer term prospect than a full scale GFR and because there is no modern data available for larger scale helium-cooled reactors, given that most recent larger scale HTRs were both shut down in 1989 (THTR 300 in Germany and Fort St. Vrain in the USA). It is worth noting that impurity levels are likely to be higher in a full scale GFR.

The “maximum” impurity levels for HTR-10 have been recommended for the non-inert species present in air i.e., nitrogen, oxygen, water vapor and carbon dioxide. The lower “expected” impurity levels have been recommended for the other non-inert impurities. In particular, carbon monoxide and methane are expected to be lower on account of the lack of graphite moderation in ALLEGRO versus HTR-10. Dalton’s Law has been used to simulate in experiments at atmospheric pressure, the impurity concentrating effect of the 70 bar pressure intended for ALLEGRO. The concentration and partial pressure data are presented in Table 2 below. In the tests presented in this work, the concentration of impurities is corresponding to the values in Table 2 at 1 bar, except the H₂O that was 60 ppm instead of 70 ppm, and it was achieved in our device using pre-mixed gas cylinders.

A galvanic cell device (ZIROX SGM5-EL) was installed at the output of the TAG to measure the oxygen concentration in the exhaust gas. A scanning electron microscope (Philips XL305) was used to analyze the sample’s surface before and after the tests.

Table 2: Recommendation for concentrations and partial pressures of oxidising species anticipated in ALLEGRO GFR helium gas coolant [13]

Impurity	Concentration (ppmv)		Partial Pressure (Pa)
	At 70 bar	At 1 bar	At 1 bar & 70 bar
H ₂	3	210	21
CO	3	210	21
N ₂	2	140	14
O ₂	1	70	7
H ₂ O	1	70	7
CH ₄	1	70	7
CO ₂	1	70	7

3. Results

The measurements with the benchtop balance did not show any change between the initial and the final mass of the samples at 900 °C and 1200 °C. On the other hand, according to the TGA results, the same samples underwent a mass gain between 0.01 and 0.03 mg for the ground and as manufactured samples at 900 °C, while the smooth samples maintained the same weight. The SEM imaging did not show the presence of SiO₂ on the sample surface. At 1200 °C the mass gain was between 0.05 and 0.1 mg for the ground and as manufactured samples, while the smooth samples did not show an appreciable mass gain. The thermogravimetric measurements are in Figure 2, 3, 4. The EDS analysis pointed out the presence of silicon oxide particles on the surface of the samples oxidized at 1200 °C for 20 hours.

At temperatures higher than 1200 °C, the TAG measurements recorded mass loss for any sample tested, as showed in Figure 3. A different surface morphology is visible comparing the SEM images of the samples oxidized at 1200 °C with the one oxidized at 1300 °C. In particular, at the higher temperatures the samples present a degraded surface with pits and pores, as noted in Figure 5 and Figure 6.

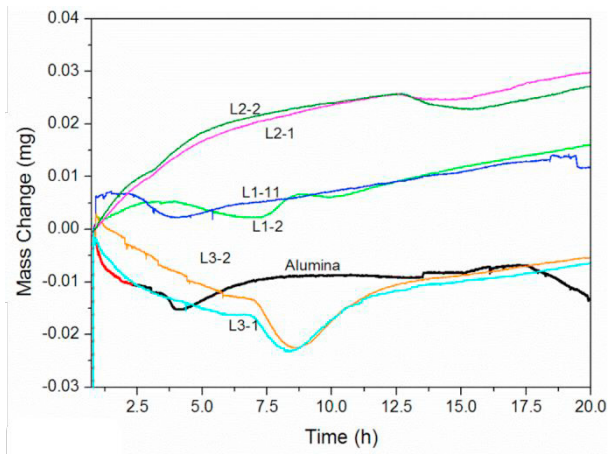


Figure 2: Thermogravimetric curves of tests performed at 900 °C.

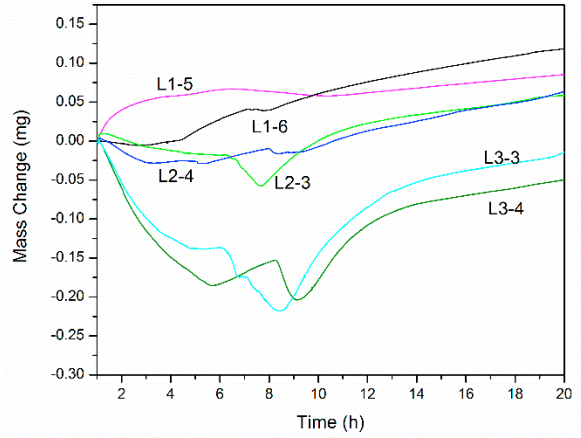


Figure 3: Thermogravimetric curves of tests performed at 1200 °C.

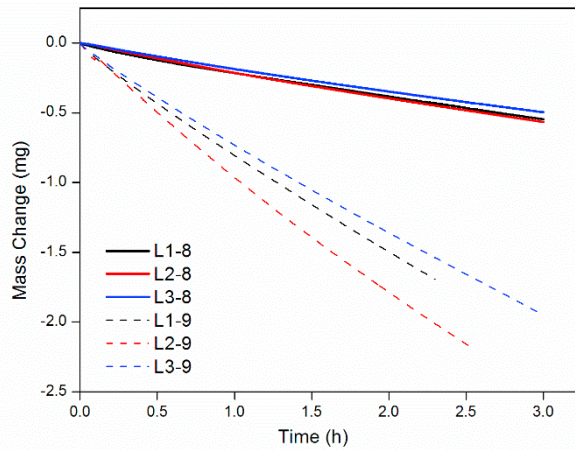


Figure 4: Thermogravimetric curves of tests performed at 1400 °C (full line) and 1500 °C (dashed lines).

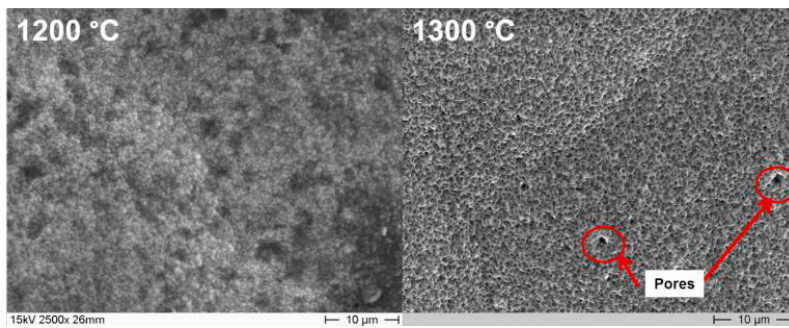


Figure 5: SEM micrograph of the surface of sample oxidized at a) 1200 °C and b) 1300 °C.

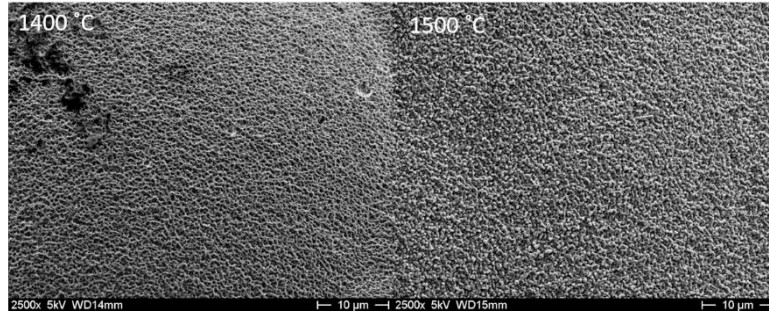


Figure 6: SEM micrograph of the surface of sample oxidized at 1400 °C and 1500 °C after 3 hours.

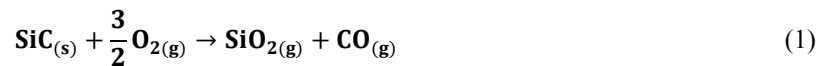
In Table 3 the linear constants calculated fitting the TGA data are presented for the experiments performed at temperatures higher than 1200 °C, where linear mass loss was detected.

Table 3: Linear constants calculated with the TGA mass loss data

Sample name	Temperature (°C)	Linear Constant k_1 (mg/cm ² h)
L2-5	1300	-0.0122
L2-6	1300	-0.0099
L1-8	1400	-0.0292
L2-8	1400	-0.0321
L3-8	1400	-0.0276
L1-9	1500	-0.1182
L2-9	1500	-0.1450
L3-9	1500	-0.1079

4. Discussion

Silicon carbide undergoes active or passive oxidation depending upon oxidant concentration and temperature [14]. In the case passive oxidation occurs, a dense and protective SiO₂ oxide scale forms on the SiC surface causing mass gain, as shown in (1).



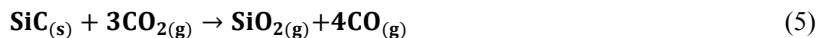
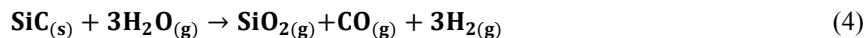
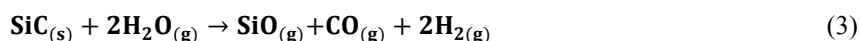
At lower oxidant partial pressures and higher temperature, active oxidation occurs and SiC decomposes into SiO and CO gases, as described by (2), without forming any protective oxide scale and undergoing mass loss.



The reaction of silicon carbide with oxygen was largely studied in the literature, but little work was done to investigate the behavior of SiC in helium and impurities atmosphere.

Kim et. Al. [15] performed tests of CVD and CVI SiC at 900 and 950 °C for 250 hours in impure helium without oxygen and carbon monoxide (200 ppm H₂, 2-10 ppm H₂O, 50 ppm CO, 20 ppm CH₄). The atomic force microscope (AFM) analyses performed [15] did not show a significant change of the surface before and after oxidation, while the XPS indicated the presence of a nanometers thick SiO₂ oxide layer. This is probably similar to the silica

thickness developed on our samples surface at 900 °C: at this temperature, a weight gain was detected with the TGA for most of the samples, while the benchtop balance did not record any change. SEM analyses on the cross section did not show any oxide, probably due to the oxide thickness, which was too low for the SEM resolution. Nogami [16] tested SiC composites at 1000 and 1200 °C in helium with 1500 ppm oxygen by means of a TGA and detected passive oxidation. Balat-Pichelin et Al. [17] performed experiments and calculations to define the transition temperature (T^{p-a}) between passive and active oxidation of α and β -SiC in helium and oxygen atmosphere. The Table 1 of [17] reports that for 10 Pa oxygen partial pressure, the theoretical T^{p-a} was 1333 °C for α -SiC, while it was 1433 °C for β -SiC. They also calculated the mass loss rate between 1377 °C and 2000 °C, and the results are comparable with the linear constants calculated in this work. The profilometry tests performed in [17] are also in accordance with our SEM images: both show a rougher and uneven surface (Figure 5) when active oxidation occurs. The same group [18] calculated the partial pressure of the gases produced during the oxidation of SiC and defined the T^{p-a} corresponding to the point where the P_{CO} equals the P_{SiO} , which resulted 1027 °C for 0.2 Pa P_{O_2} and 1127 °C for 2 Pa P_{O_2} . The transition temperature observed in our experiments with 140 ppm O_2 is between 1200 and 1300 °C, which is lower than the values published by Balat-Pichelin et al. [17]. This can be explained considering that our atmosphere contains more gas species that can react in the gas mixture. In order to understand the behavior of the gas, the thermodynamic equilibrium of the species in Table 2 at 1 bar was calculated with the Fact-sage and the FactPS database [19]. The results showing the partial pressures of the species in our mixture depending on the temperature are in Figure 7. According to the calculations, the oxygen is many orders of magnitude lower than the other species. This suggests that at equilibrium the oxygen reacts with H_2 increasing the H_2O partial pressure. Traces of H_2O and CO_2 can also react with SiC according to the following reactions [20–22]:



Despite reaction (5) can occur in our tests, the reaction with steam is known to have a higher oxidation rate [22], suggesting that at 900 and 1200 °C reaction (4) is occurring. At higher temperature reactions (2) and (3) take place, leading to mass loss of the samples. This hypothesis is confirmed by a calculation performed including solid SiC with the mix of gases already shown in Figure 7. The results show that the solid SiO_2 is present up to ≈ 1215 °C, while at higher temperatures the activity of SiO_2 drops to zero and solid silica is not present anymore, addressing the transition between passive and active oxidation under these conditions.

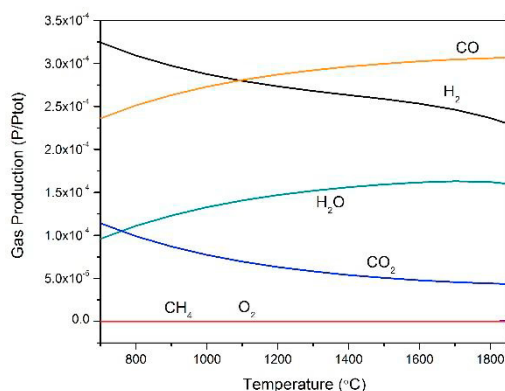


Figure 7: Fact-sage calculations of the equilibrium for the gas species at 1 bar as presented in Table 2 depending on the temperature using the FactPS database.

5. Conclusions

Tests under GFR conditions of SiC/SiC_f composites specimens provided by CEA were performed in well-defined helium/impurities gas mixture. Passive oxidation was detected at 900 °C and 1200 °C, whereas the samples underwent active oxidation and mass loss at 1300 °C, 1400 °C, and 1500 °C. The linear constants are presented for the higher temperature. The transition between passive and active oxidation was calculated using FactSage resulting ≈1215 °C, in accordance with the experimental results. Overall, the results meet the requirements for the aimed application, since the transition temperature from passive to active oxidation is 300 °C higher than the nominal working conditions of GFR.

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