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Chemical degradation of SiC/SiC composite for the cladding of gas-cooled fast reactor in case of severe accident scenarios

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ABSTRACT

High temperature oxidation was performed on structural materials made of fibres of SiC in a SiC matrix (SiC/SiC) + β-SiC coating, considered for the cladding of the gas-cooled fast reactor. Tests carried out in various atmospheres (helium, nitrogen, air) coupled to mass variation, SEM and XPS analysis enabled the study of resistance to chemical degradation of such composites from 1400 to 2300 K. Monolithic β-SiC was also studied for comparison. The degradation of the composite material was faster than the monolithic one above 1970 K due to the damage of the β-SiC coating enabling the oxidizing species to penetrate inside the composite.

1. Introduction

SiC is oxidized according to two regimes, mainly depending on the oxygen partial pressure and the temperature. During passive oxidation (Eqs. (1) and (2)) – often at low temperature and high partial pressure of oxygen – a silica layer is formed on the surface of SiC and this layer is protective slowing down the oxidation process (passivation):

$$SiC_{(s)} + 2\ O_{2(g)} = SiO_{2(s)} + CO_{2(g)} \tag{1}$$

$$SiC_{(s)} + 3/2\ O_{2(g)} = SiO_{2(s)} + CO_{(g)} \tag{2}$$

During active oxidation (Eq. (3)) – often at high temperature and low partial pressure of oxygen – gaseous SiO is produced and consequently, no passive layer is formed and significant mass loss is observed:

$$SiC_{(s)} + O_{2(g)} = SiO_{(g)} + CO_{(g)} \tag{3}$$

Active oxidation of SiC-based materials has been studied by several authors [1–12] and recently Jacobson and Myers have published a review on this topic [13]. In our recent publications [10–12] some results were presented on the oxidation behaviour of various kinds of SiC materials (monolithic α- and β-SiC, composite SiC/SiC with β-SiC coating) which was planned for cladding the fuel particles in the gas-cooled fast reactor (GFR) which is one of the future nuclear reactors belonging to Generation IV [14,15]. These materials would have to work at nominal conditions around 1000–1300 K in helium pressurized at 7 MPa. The chemical stability and especially the oxidation resistance of the cladding is one of the important properties for cladding materials since the helium coolant gas can contain a low residual oxygen partial pressure. We have determined the transition between passive oxidation (with formation of a protective SiO_2 layer) and active oxidation (with severe degradations due to the release of gaseous SiO and CO) for different SiC materials [6,10,11].

We are hereby studying what could be the consequences of an accident inside the GFR. The integrity loss of the cladding could lead to the release of gaseous and volatile fission products. The possible loadings on the cladding could be a mechanical loading, a thermal loading or a chemical loading. The mechanical loading, directly associated to the loss of the main safety function devoted to the confinement can be attributed to a very large break leading to a loss of coolant gas with the loss of the back-up pressure [16]. In case of such severe accident, the temperature can climb up to 2300 K with heating rates up to 100 K s^{-1}. The REHPTS set-up (*REacteur Hautes Température et Pression Solaire* – High Temperature and Pressure Solar Reactor), previously described [11] seems therefore the most accurate tool to simulate such fast heating rates. We used this set-up to analyse the chemical degradation of samples representative of the cladding material (SiC/SiC composite with β-SiC coating) during simulated accidental conditions in helium with a residual oxygen partial pressure. In case of severe accident, a natural circulation cooling can be used thanks to a

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heavy gas injection in the primary circuit, by means of accumulator tanks simultaneously opened when the primary pressure reaches a limit value. Calculations have shown that nitrogen can cool efficiently the core in case of failure of the forced convection [16]. Hence, we have also studied the chemical degradation of the cladding material in nitrogen and in air (in case of massive break). Samples of monolithic β-SiC were also treated under such conditions for comparison. Finally, the influence of thermal ageing by increasing the heating duration was studied, also to see if there is an influence on the kinetics rate at 1500 K and 1900 K on both composite and monolithic samples.

2. Experimental procedure

2.1. Materials

Experiments have been carried out on a SiC/SiC composite material manufactured by Snecma Propulsion Solide (Safran-SPS, France). This material involves Hi-Nicalon fibres of β-SiC from Nippon Carbon, Japan covered with a pyrocarbon interphase. The Hi-Nicalon fibre presents a low oxygen content (0.5 wt%) and consists of a mixture of SiC nanocrystals (≈5 nm mean size) and free carbon with a atomic ratio C/Si of 1.39 [17,18]. The β-SiC matrix was fabricated by chemical vapour infiltration (CVI). On one side, the surface porosity is closed by a β-SiC coating through chemical vapour deposition (CVD). This very dense layer (density 3.2 g cm^{-3} and porosity <1%) prevents the oxygen from diffusing toward the material, and is effective when temperature is sufficiently high (around 1400 K in air) to seal the residual cracks with silica [19,20]. The density of the final composite material is estimated around 2.8 g cm^{-3} with an open porosity around 7% and a closed one of 2%. The size of the squared samples was around 25 × 25 mm with a thickness of 1.5 mm and an initial mean mass of around 1.5 g. Other experiments were carried out on monolithic samples of β-SiC in order to compare with the composite. These samples have been fabricated by Rohm & Haas (USA) by CVD process in a temperature range 1470–1570 K. The composition of this material is in wt%: Si 67.9, C 30.6, N < 0.1, O < 0.1, and the atomic ratio C/Si around 1.05 evidences a nearly stoichiometric material. The density of this material is around 3.2 g cm^{-3} with a densification level higher than 99%. The coupons of this material was shaped into approx. 25 × 25 × 2 mm sample with an initial mean mass of around 4.0 g.

Fig. 1 presents pictures and SEM images of the reference samples for both materials.

2.2. Oxidation procedure and material characterization

Samples were oxidized for 10 min. at constant temperature inside the REHPTS, according to the same procedure previously described [10–12]. This reactor is placed – in the focal volume of the 5 kW solar furnace of Odeillo – in order to have the sample located 25 mm above the focus of this solar furnace, thus elevated temperatures on materials such as SiC may be obtained at very fast rate (up to 100 K s^{-1}) on a homogeneous 10 mm diameter area. A monochromatic (5 μm) optical pyrometer and two mirrors allow to measure the surface temperature of the sample through a fluorine window. The spectral normal emissivity taken for SiC is 0.90 at this wavelength and it does not change during passive or active oxidation, silica presenting the same emissivity as SiC at this wavelength. The accuracy of the temperature measurements is going from 1400 ± 15 K to 2300 ± 25 K. Composites samples were oxidized in helium and in air, monolithic samples were oxidized in helium and in nitrogen. Helium (He U, Air Liquide with 20 ppm. O_2 impurity grade) was used at a total pressure of 10^5 Pa which gives an oxygen partial pressure of 2 Pa. Experiments were performed using a standard quality of nitrogen (N_2 U, Air Liquide with 5 ppm O_2 impurity grade). Experiments in air were conducted by opening the reactor to the surrounding atmosphere before heating, the total pressure was therefore lower – around 8.7 × 10^4 Pa – and the pO_2 is equal to 1.7 × 10^4 Pa due to the fact that our laboratory is located at 1500 m altitude. The gas phase composition inside the reactor is checked by a mass spectrometer (©Pfeiffer Omnistar Vacuum GSD 301) and the oxygen grade given by the provider was verified using an oxygen analyser. In situ analysis of the gaseous phase was performed using the mass spectrometer enabling to follow the variation of the intensity corresponding to the gaseous species CO (at $m/e = 28$) and SiO (at $m/e = 44$). Mass variation was measured by weighing the samples before and after oxidation (balance accuracy is 10^{-4} g) converted to percentage and rates of mass change are reported to the initial surface of the sample and expressed in

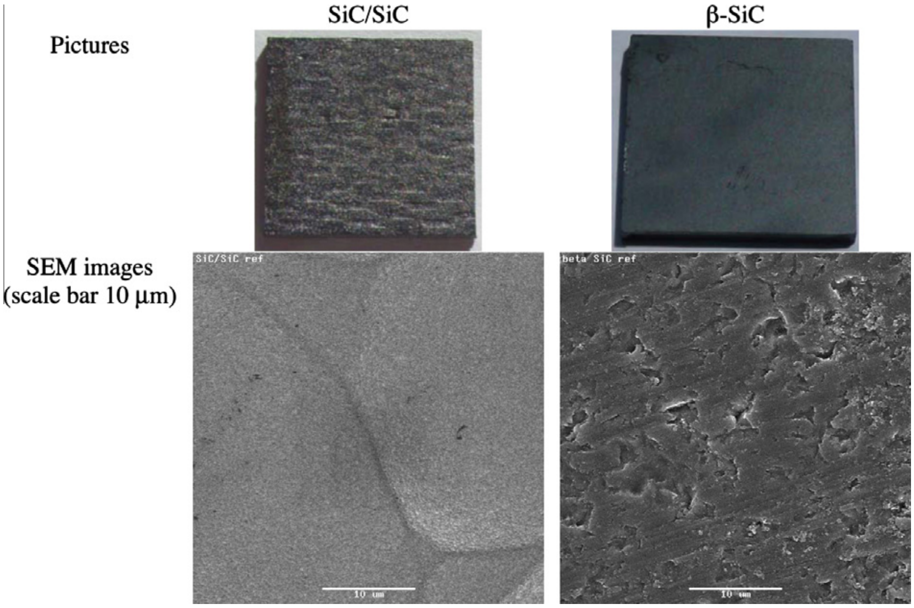

Fig. 1. Pictures and SEM images of reference samples: SiC/SiC composite and monolithic β-SiC.