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# Oxidation at high temperatures in steam atmosphere and quench of silicon carbide composites for nuclear application

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## HIGHLIGHTS

- SiC produces several times less hydrogen than Zircaloy in case of accident.
- SiC tube maintained coolable shape after quench tests at 2000 °C.
- Oxidation tests in steam at 1600 °C showed bubbles formation on SiC surface.

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## ABSTRACT

After the Fukushima accidents, the need for a fuel-cladding system with better performance in accident conditions has been raised. Silicon carbide and its composites are nowadays candidates for replacing zirconium alloys as cladding material for light water reactors. This paper reports about oxidation and quench tests of relevant silicon carbide samples at temperatures up to 2000 °C in steam atmosphere. During the experiments the reaction gases were analyzed by mass spectrometry, and after the tests the samples were characterized by means of optical microscopy, scanning electron microscopy, as well as XRD and X-ray tomography. Oxidation results showed good resistance of SiC composite despite the formation of bubbles on the surface. The quench tests proved the samples retained their original shape.

## 1. Introduction

Since the beginning of the nuclear industry, efforts to improve the fuel performance of light water reactors (LWR) have been made by industry and research institutions. After the severe accidents at the Fukushima Daiichi Nuclear Power Station in 2011, a need for enhanced system safety has been demonstrated. The actual fuel rods, which consist of zirconium alloy cladding coupled with uranium dioxide, or a mixture of uranium and plutonium dioxide fuel, are mature and reliable during operation. However, their behavior in the case of extremely rare accident events raises significant concerns. In particular, the strongly exothermic interaction of the cladding with steam produces free hydrogen. Combustion of hydrogen worsened the Japanese accidents, causing explosions and destruction of the reactor building. This event underlined the evidence of the need for an improved cladding, which would have a better performance under accident conditions maintaining an excellent behavior during operation.

By definition, accident tolerant fuels (ATF) are fuel-cladding systems, which could tolerate loss of active cooling in the core for longer periods of time than the currently adopted systems, while keeping an acceptable or even better performance during normal operation. Silicon carbide is a suitable candidate for substituting the actual cladding (Hallstadius et al., 2012): it combines high performance in extreme environments (Stempien, 2011; Alpettaz et al., 2012; Lee et al., 2013) and chemical compatibility with the fuel system (Katoh et al., 2011). For many years, silicon carbide has been tested as a possible material for nuclear power plants (Snead et al., 2007). Today it is being investigated as a structural material in both light water and high temperature reactors, and different designs are studied worldwide. The monolithic SiC behaves as a ceramic material, thus undergoing brittle fracture. The combination of monolithic SiC with SiC fibers in a $SiC/SiC_f$ composite leads to a pseudo-ductile behavior. For this reason, the use of a $SiC/SiC_f$ composite seems to be very promising. The SiC fibers have been

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improved over the last years, going through three different fiber generations in order to reach an as close as possible stoichiometric composition (Bunsell and Piant, 2006). Indeed, the presence of the silicon oxycarbide phase, which was typical in the first fiber generation, caused instability of the material, in particular at high temperatures and under irradiation. Although the second fiber generation had overcome this problem, the presence of a large amount of free carbon was still affecting the oxidation and creep resistance (Bansal and Lamon, 2015). The third generation of SiC fibers produced was nearly stoichiometric and therefore the behavior was comparable to that of the SiC bulk material. To date, Hi-Nicalon Type-S and Tyranno SA SiC fibers are known to be stable under irradiation (Bansal and Lamon, 2015). Assessment of these composites at very high temperatures and under accident conditions is still on-going.

In this paper, oxidation tests of SiC–SiC$_f$ cladding samples are described at temperatures between 1600 °C and 1800 °C in steam and quenching in water at temperatures of up to 2000 °C. The response to these scenarios, including hydrogen production, has been measured.

## 2. SiC oxidation in steam

The oxidation between silicon carbide and steam at high temperatures can be categorized into two different reactions, called passive and active oxidation. Active oxidation occurs in the case of very low water vapor partial pressures (Opila and Jacobson, 1995) (<10 Pa at 1427 °C). In the case of higher oxidant partial pressure, the SiC undergoes reaction (Eq. (1)), developing a dense protective layer of silica ($SiO_2$):

$$SiC + 3H_2O = SiO_2 + 3H_2 + CO \tag{1}$$

In case passive oxidation occurs, the silicon carbide oxidation behavior follows the linear-parabolic model of Deal and Grove (Deal and Grove, 1965; Costello and Tressler 1986). At the same time, silica volatilization occurring via the following reactions degrades the oxide scale:

$$SiO_{2(s)} + 2H_2O_{(g)} \rightarrow Si(OH)_{4(g)} \tag{2}$$

$$SiO_{2(s)} + H_2O_{(g)} \rightarrow SiO(OH)_{2(g)} \tag{3}$$

$$SiO_{2(g)} + \frac{1}{2}H_2O_{(g)} \rightarrow SiO(OH)_{(g)} + \frac{1}{4}O_{2(g)} \tag{4}$$

Volatilization is described by a linear constant, which is combined with the parabolic constant in the so-called para-linear behavior, which was formulated for $Cr_2O_3$ by Tedmon (1966) and applied for the first time to model the oxidation of SiC by Opila and Hann (1997). This is defined by the paralinear equation (Eq. (5)), where $k_p$ is related to the parabolic oxidation of the SiC, whilst $k_l$ describes the volatilization.

$$\frac{dx}{dt} = \frac{k_p}{2x} - k_l \tag{5}$$

In this relation, $x$ is the oxide thickness and $t$ the time. The parabolic constant $k_p$ has been demonstrated to be proportional to $P(H_2O)$ with a power law exponent of one, whilst the linear constant $k_l$ is proportional to the velocity ($v$) and the total pressure $P_{tot}$ (Eq. (6)) (Opila and Hann, 1997).

$$k_l \sim \frac{v^{1/2}P(H_2O)^2}{P_{tot}^{1/2}} \tag{6}$$

Different authors have investigated the oxidation of SiC in steam. Jorgensen et al. (1961) tested SiC in water at up to 1514 °C using a thermobalance. In his work, he stated that the oxidation rate of silicon carbide depends on the water vapor partial pressure. Narushima et al. (1990) tested CVD–SiC with a thermobalance (TGA) at up to 1650 °C in wet oxygen (10 kPa steam) and suggested that the rate-controlling step is oxygen diffusion in the parabolic regime based on the activation energy found. Opila (Opila and Smialek, 1999) developed the paralinear kinetic model and mapped out the conditions to apply it, elucidating the strong dependency of the volatilization on the external conditions (Opila, 2003). Oxidation tests at high pressures of up to 2 MPa and temperatures of as high as 1700 °C have been performed by Oak Ridge National Laboratory (ORNL) (More et al., 2000; Terrani et al., 2014; Farmer et al., 2014). It was found that at high steam partial pressures, the oxide scale develops porosity due to the formation of CO gases, degrading the silica protective properties. This non-protective porous layer increases with time, leaving vitreous silica of constant thickness on the SiC.

The oxidation of SiC is a diffusion-controlled reaction, although no agreement has been found regarding the species diffusing. It has been stated by many authors that the presence of water vapor enhances the oxidation rate. This has been explained considering that the $H_2O$ molecule is smaller than the $O_2$ molecule (276 versus 320 pm at 700 °C) (Presser and Nickel, 2008), and it reacts with the silicon–oxygen network forming immobile SiOH groups (Doremus, 2001). Moreover, the $H_2O$ molecule alters the $SiO_2$ network and increases the diffusion of oxidant species (Irene, 1977). The plot of the logarithm of the parabolic rate constant $k_p$ versus the logarithm of the partial pressure of water provides information on the oxidant species. In the case SiC oxidizes in oxygen atmosphere, the slope indicates diffusion of molecular oxygen ($n = 0.5$). In the case of water, the $n$ coefficient has higher value. The most reliable explanation yields to parallel diffusion of a molecular and an ionic hydrogen-containing phase ($H_2O$ and $OH^-$) (Presser and Nickel, 2008).

A third oxidation phase has been noted by different authors (Narushima et al., 1994; Terrani et al., 2014), which consists in the development of bubbles on the surface and therefore implies degradation of the protective silica scale.

## 3. Experimental procedure

### 3.1. Samples

Samples of Ceramic Matrix Composite (CMC) silicon carbide/silicon carbide fibers from two producers (CEA and CTP$^{LLC}$) were used to perform oxidation and quench tests. A summary of the samples used is shown in Table 1. The cladding design developed by CEA laboratories (Bansal and Lamon, 2015; Buet et al., 2012) consists of three braided layers (with 45° of orientation) of Hi-Nicalon S fibers provided by Nippon Carbon, reinforced with SiC CVI matrix. To improve the mechanical behavior of the composite, which is controlled by the matrix–fiber bonding, the interface between the fiber and the matrix has been refined with pyrocarbon, which is known to be the best interphase; a layer ≈ 20–30 nm thick was deposited on the SiC fibers prior to the matrix infiltration. As protection, an external 50 μm thick CVD layer was applied. 21 tube samples of a length of 20 mm, an external diameter of 9.5 ± 0.1 mm and a wall thickness of 0.89 ± 0.01 mm have been provided by CEA (Table 1).

**Table 1**
Samples used for the experiments.

| Producer | Number of samples | Temperature (°C) | Quench |
|---|---|---|---|
| CEA | 10 | 1600 | × |
| CEA | 5 | 1700 | × |
| CEA | 6 | 1800 | × |
| CTP | 4 Monolith | 2000 | √ |
| CTP | 4 Composite | 2000 | √ |