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Original Article

# High temperature oxidation of two- and three-dimensional hafnium carbide and silicon carbide coatings

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**Abstract**

The difficulty in using C/C composites as structural components above 2000 °C in an oxidizing atmosphere is their poor lifetime. The solution proposed here consisted in combining two refractory carbides, hafnium and silicon carbides, in coating with a complex architecture, named a three dimensional coating, over a C/C substrate. Such a coating protects the C/C composite at 2000 °C under air. The oxidation of the coating leads to the formation of a $Si_xO_yHf_z$ hafnium-containing silicate liquid, combined with $HfO_{2(s)}$. This liquid limits oxygen diffusion more than pure $SiO_2$ does, so it is a better protection against oxidation. Furthermore, $HfO_{2(s)}$ acts as a frame holding $Si_xO_yHf_z$ in place. From these results, an oxidation mechanism is proposed and discussed.


*Keywords:* HTC; Oxidation; Carbides; Refractories; Hafnium

## 1. Introduction

C/C composites (carbon fibers embedded in carbon matrices) exhibit a poor lifetime under an oxidizing atmosphere; the carbon fiber starts to be oxidized under air at a temperature of 400 °C.[1] In order to protect composites from oxidation, many coatings made of Ultra High Temperature Ceramics (UHTCs) have been tested. It is known that they can resist to extreme heat flux and high mechanical stresses.[2] For example, Clougherty et al. have studied oxidation of diborides $HfB_2$, $ZrB_2$ $TiB_2$ and a mixture of $HfB_2$–SiC.[3] The oxidation mechanism model of these coatings has been studied by Parthasarathy et al.[4] who proposed a mechanistic model that simulates the oxidation behavior of the diborides in the temperature range of 1000–1800 °C. Among the studied carbide-based coatings, an HfC/SiC dual layer developed by Wunder et al. has shown promising oxidation protection for PyC-coated C/C composites at temperatures up to 1450 °C.[5] Besides, Baklanova et al. highlighted the fact that HfC/SiC-coated carbon fibers exhibit a higher oxidation resistance at 2000 °C than the initial HfC-coated carbon fibers.[6] Wang et al. have determined that SiC/HfC/SiC is an interesting coating to protect carbon/carbon composites with a mass loss of only 2.3% after oxidation at 1500 °C. They have also characterized a stable glassy phase composed of $HfSiO_4$ which could protect C/C composites.[7]

In the present work, two carbides were selected. SiC has been used in many works; it allows protection against oxidation until 1650 °C by forming a $SiO_2$ layer.[8] It is the best diffusion barrier against oxidation below 1400 °C.[1] But, above 1650 °C under air the oxidation becomes active and all the protection is lost. In spite of a high melting point (3890 °C), HfC is actively oxidized at low temperature, from 400 °C to 500 °C, forming porous $HfO_2$. Its oxidation behavior has been studied by Shimada et al.[9] Although not protective, this oxide has the advantage of being refractory with a melting point of 2810 °C and has a lower vapor pressure than $SiO_2$.[4] The aim of the present study was to combine these two carbides to find a synergetic effect: a refractory coating that allows a good oxidation resistance. Three kinds of samples, (i) a monolithic HfC/SiC samples type consisting of coated and sintered powder, and two C/C composites with $(HfC/SiC)_n$ multilayer coating types, (ii) 2D and (iii) 3D, were prepared and patented.[10,11] In the 2D $(HfC/SiC)_n$ multilayer coatings delamination can occurs and layers could slide over each other during oxidation at high temperature. The 3D $(HfC/SiC)_n$ multilayers

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Table 1
Sample characteristics overview.

| | Sample A | Sample B | Sample C |
|---|---|---|---|
| Sample kind | Monolithic | 2D (10 layers) | 3D + 2D (10 layers) |
| Sample composition | HfC/SiC | C/C substrate + $(HfC/SiC)_5$ | C/C substrate + $(HfC/SiC)_5$ |
| Way of synthesis | FBCVD + SPS | CVD | CVD |

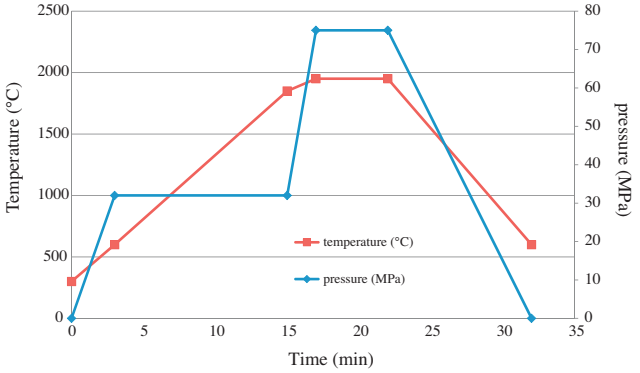


Fig. 1. Pressure and temperature cycles of spark plasma sintering.

comprise SiC whiskers deposited as a first layer. As explained by Chu et al., SiC nanowires (or whiskers in our case) increase the mechanical properties of a coating such as hardness, elastic module and fracture toughness and improve the oxidation protection of the sample.[12,13] These improvements are due to a mechanism including whiskers pullout, micro-crack deflection and better interface interaction, whiskers acting as attachments of sub-layers.

Then samples were characterized after high temperature oxidation. This characterization of the oxidized samples allowed us to propose an oxidation mechanism.

## 2. Experimental procedure

### 2.1. Monolithic sample

The monolithic freestanding sample (named sample A, Table 1) was prepared by following two steps.

HfC powder with a $d_{50} = 35\ \mu m$, was first coated with 1 μm of SiC by fluidized bed chemical vapor deposition (FBCVD) by Lifco Industrie (France). Then this core–shell powder was sintered by spark plasma sintering (SPS). Sintering parameters were: temperature of 1950 °C, pressure of 75 MPa and dwell time of 5 min, following cycles presented in Fig. 1.

The machine was a Dr Sinter 2080 from Syntex (Japan). The final sample was a cylinder with a diameter of 15 mm and a thickness of 6 mm.

### 2.2. Multilayer coating made by CVD

The other kinds of samples (sample B and sample C, Table 1) consisted in $(SiC/HfC)_n$ multilayer coatings over C/C substrates prepared by low pressure chemical vapor deposition (CVD) at 1000 °C and 5 kPa.[11] Samples B and C have the same size as

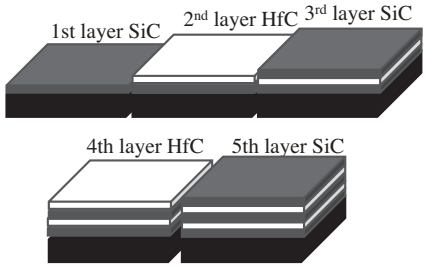


Fig. 2. Structure scheme of the 5 first layers of sample B corresponding to 2D structure coating.

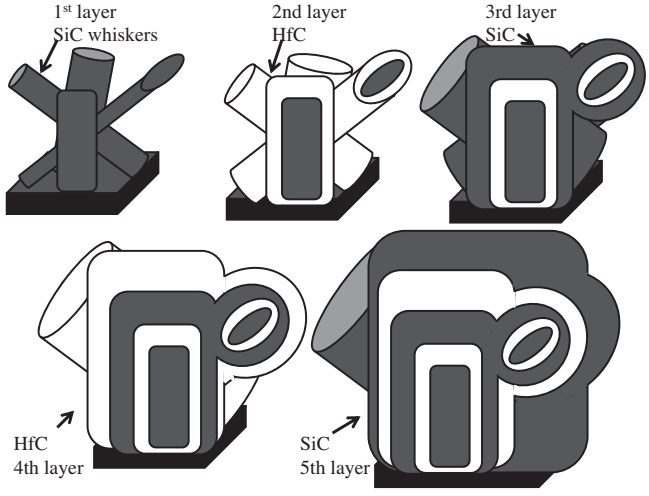


Fig. 3. Structure scheme of the 5 first layers of sample C corresponding to 3D structure coating.

sample A. The device used was composed of a hot-wall CVD reactor and a chlorinating device. $HCl_{(g)}$ reacted at 700 °C with metallic $Hf_{(s)}$ to form $HfCl_{4(g)}$ in the chlorinating device. The hafnium metal was an electrolytic grade $Hf_{(s)}$ supplied by Areva. $HfCl_{4(g)}$ precursor was simultaneously injected with argon as a carrier gas and reacts with $CH_{4(g)}$ and $H_{2(g)}$ in the CVD reactor to give HfC coating. The SiC layers were classically made from methyltrichlorosilane and hydrogen. The MTS was supplied by Sigma–Aldrich and its purity was superior to 97%.

Sample B consisted of a classical bi-dimensional (2D) coating made of ten alternated layers of SiC and HfC, according to Kaplan's patent.[14] A structure scheme, corresponding to the five first layers, is presented in Fig. 2. The five last layers are identical to the five first ones.

Sample C consisted of five alternated layers of HfC and SiC with a three-dimensional (3D) arrangement and another five alternated layers of HfC and SiC with a two-dimensional arrangement, according to our patent.[11] In this 3D structure, the