

## PROTECTION AGAINST OXIDATION, BY CVD OR SPS COATINGS OF HAFNIUM CARBIDE AND SILICON CARBIDE, ON CARBON/CARBON COMPOSITES.

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### Abstract

*The hafnium carbide compound is an ultra high refractory ceramic; as a result it could be of interest for the protection of carbon/carbon composites against oxidation at high temperatures. However HfC and most of metallic carbides present a non stoichiometric composition with carbon vacancies. As a consequence, the oxidation resistance is poor at low temperatures (500-1000°C). In order to overcome this main drawback the HfC can be associated with silicon carbide (SiC) presenting a better oxidation resistance at lower temperatures.*

*Two coating routes have been studied; the first one is the Chemical Vapour Deposition which enables to obtain very thin coatings and the second one is the Spark Plasma Sintering technique which permits to get new microstructures of coatings.*

*On first hand, this study describes the CVD conditions for the deposition of HfC from the metallic hafnium pellets to get hafnium chlorides followed by the reduction of the chlorides by H<sub>2</sub> and the deposition of HfC with the methane as carbon precursor.*

*In an other hand, SPS has permitted to sinter, on carbon substrate, ultra high refractory ceramic powders with a significant amount of SiC. The sintering conditions to obtain an uncracked coating will be presented as well as microstructures and oxidation tests.*

### 1 Introduction

Hafnium carbide is one of the most refractory compound ( $T_f = 3900^\circ\text{C}$ ), stiff and tough. HfC could be of interest to protect C/C composites in severe oxidation or ablation conditions <sup>[1]</sup>. However HfC such as most part of metallic carbides has a very poor oxidation resistance <sup>[2]</sup>, its oxidation starts at 450°C. In order to overcome this main drawback HfC could be associated with a carbide (ex: SiC) presenting a better oxidation resistance <sup>[1,3]</sup>. HfC and SiC coatings, dense and chemically pure, are obtained by Chemical Vapour Deposition (CVD) technique <sup>[1,3]</sup>.

In this present study two CVD techniques have been used to get two different types of coatings. Low pressure CVD has been chosen to get a HfC and SiC alternate multilayer coating on a C/C composite. In another hand Fluidized Bed CVD (FBCVD) gives an individual SiC coating on each HfC powder particle. This coated powder has been sintered on C/C substrate by Spark Plasma Sintering.

Thermal behaviour under air of those two types of coatings has been investigated using an arc image furnace.

## 2 Experimental

### 2.1 Multilayer coatings on C/C substrates by low pressure CVD.

The experimental device is composed of two kilns. The first one (figure 1) is the chlorination device in which the reaction of metallic Hf with HCl at 700°C occurs, which enables to produce the hafnium chloride (HfCl<sub>4</sub>). This chloride is carried away to the CVD kiln, shown on figure 2, in a pipe heated at 500°C in order to avoid any condensation. A high temperature gas gate can be closed in order to isolate the chlorination device from the CVD kiln. The C/C substrates are placed in this CVD kiln. HfC precursors are hafnium chloride HfCl<sub>4</sub> and methane CH<sub>4</sub>.

This device enables to get, in one step, a multilayered coating (SiC/HfC)<sub>n</sub>. To switch from HfC to SiC the high temperature gas gate is closed between the chlorination device and the CVD kiln. At that point, MTS (Méthyltrichlorosilane) carried away by H<sub>2</sub> is the SiC precursor.

Working temperature is 1000°C. For each layer two hours are necessary to obtain a suitable and adherent coating. Low pressure CVD (5 kPa) enables to get a good infiltration of the first SiC layer which leads to a good mechanical behaviour of the coating.

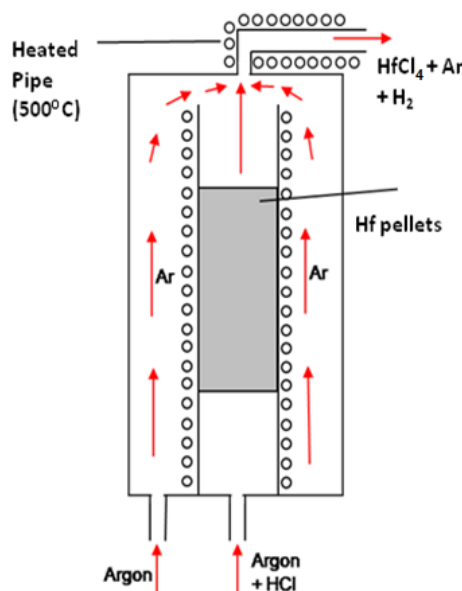


Figure 1 : Chlorination device

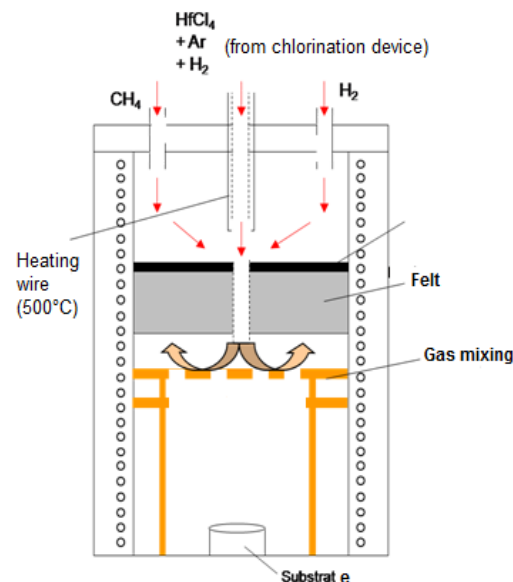


Figure 2 : CVD kiln

The C/C samples are disks of 13 mm in diameter and 5 mm in thickness. The C/C is a dense 3D ( $d > 1.85$ ). Before the CVD treatment the samples are for one part cleaned in an ultrasonic bath of ethanol during 30 minutes then dried and for the other part dipped in a metallic particles slip. Those particles are expected to catalyze the first layer of SiC in order to get SiC whiskers as first layer<sup>[4]</sup>.

## 2.2 C/C protected by sintered coated powder.

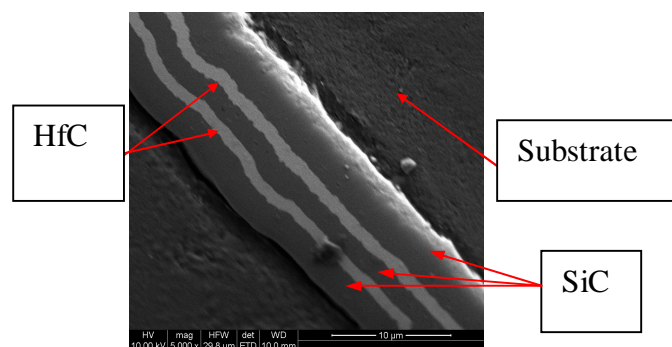
In the case of HfC powder coated by SiC, starting powder exhibits a  $d_{50}=35\mu\text{m}$ , the SiC coating is achieved by fluidized bed CVD. Hexamethyldisilane is used as a precursor to enhance the SiC coating on HfC powder. The experiment is run under  $\text{H}_2$  (transport and reduction) and under  $\text{N}_2$  (fluidization gas) at  $900^\circ\text{C}$ . It takes 12 hours to get suitable coatings. Thickness of SiC coating is about  $1\mu\text{m}$ .

Then, this coated powder is directly sintered on C/C substrates by Spark Plasma Sintering device. Sintering conditions are: temperature  $1950^\circ\text{C}$ , pressure 75 MPa and dwell time of 5 minutes. The machine is a Dr Sinter 2080 from Syntex (Japan).

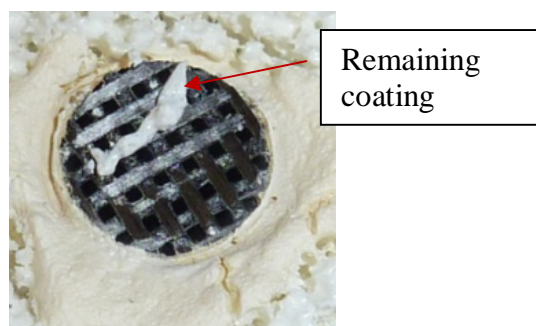
Those two coating concepts have been tested under air at temperatures until  $2050^\circ\text{C}$  in an arc image furnace at the CEA CESTA. Cycle, in terms of heat flow, is the same for all the tests and enables to reach temperatures, measured by thermocouples, of  $1600^\circ\text{C}$  after 50 seconds and  $2050^\circ\text{C}$  after 200 seconds.

## 3. Results and discussions

### 3.1 Multilayer coatings on C/C substrates by low pressure CVD.



**Figure 3:** SEM micrography of an alternate multilayer (5 layers) SiC/HfC coating on C/C substrate obtain by CVD.

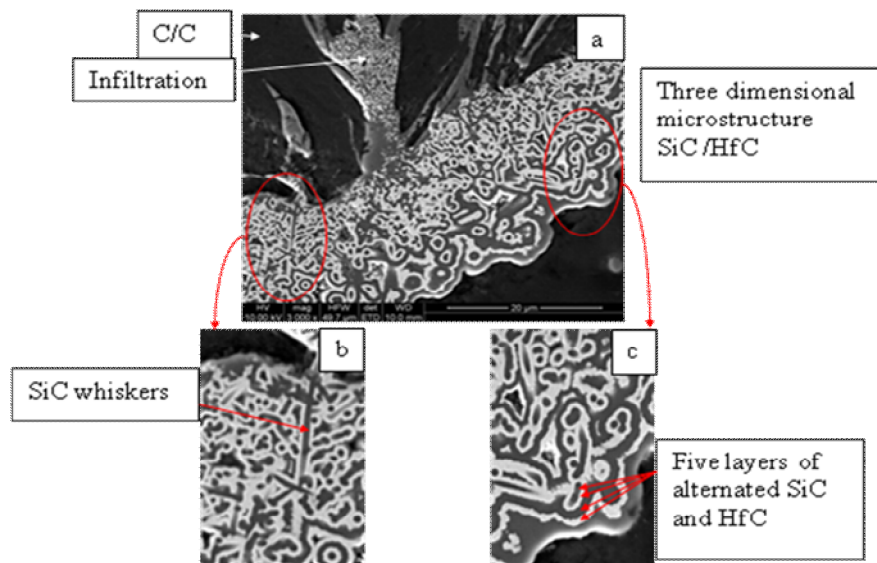


**Figure 4:** Pictures of a C/C coated with 10 layers coating after a cycle of 205 s, maximum temperature  $2050^\circ\text{C}$ .

Figure 3 shows that no cracks inside or between the layers can be seen. SiC/HfC layers are distinct and alternating and they exhibit a thickness of  $2\mu\text{m}$ . This individual thickness has been determined in order to avoid debonding. This was justified by the lack of reactivity between C/C and SiC and between SiC and HfC. The coating is fully dense and follows the C/C surface. It's even infiltrated inside the open porosity of the C/C substrate.

Oxidation tests have shown that a sample made of a C/C coated with 10 layers (5 SiC, 5 HfC) total thickness of  $20\mu\text{m}$ , begins to be destroyed after 130 seconds which corresponds to a temperature of  $1800^\circ\text{C}$ . The sample is totally destroyed after 160 seconds which corresponds to a temperature of  $1900^\circ\text{C}$ . Figure 4 shows the sample after 205 seconds which corresponds to a temperature of  $2050^\circ\text{C}$ , one can be seen that there is almost no coating left, the C/C

sample appears unprotected. In order to get a coating which can be used during several seconds at 2000°C, a special treatment which brings to a new microstructure has been realised [5].



**Figure 5:** SEM micrograph of an alternate multilayer (5 layers) SiC/HfC coating on C/C substrate (with metallic catalyst) obtain by CVD.



**Figure 6:** Pictures of a C/C coated with 10 layers coating after a cycle of 205 s, maximum temperature 2050°C.



**Figure 7:** Pictures of a C/C coated with 10 layers coating after a cycle of 370 s, maximum temperature 1900°C.

Figure 5 shows the microstructure of a five layers coating obtained with a sample that have received a layer of catalyst metal particles before the CVD treatment. In such a microstructure the first layer of SiC grows as SiC whiskers of a few microns of diameter. It looks like a “forest of whiskers” over which the second layer is deposited. This second layer composed of HfC matches perfectly the SiC whiskers. Then the third layer composed of SiC covers the

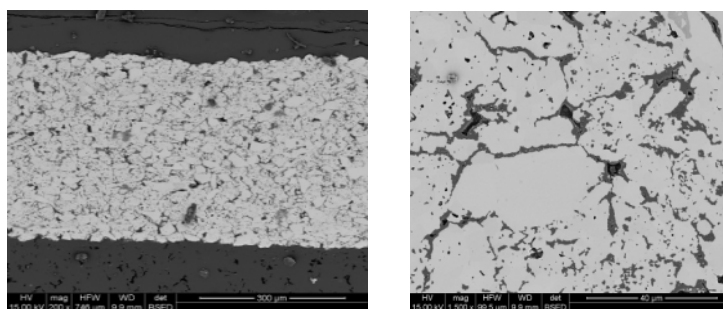
previous ones and so on to a total of five layers. This microstructure can be considered as a three dimensional microstructure compared to the one shown in figure 3 in which the layers are stacked on each other which can be considered as a two dimensional microstructure. As the microstructure obtained without catalyst this one is fully dense with no cracks inside or between the layers and the coating is still infiltrated inside the open porosities of the C/C sample.

In order to investigate the oxidation behaviour a ten layers coating has been realised. Figure 6 shows the sample after the oxidation test total time of 205 seconds which corresponds to a temperature of 2050°C. The coating is still efficient but the first defects appear and the C/C can be seen underneath the coating. This behaviour must be compared with the one of the two dimensional coating shown in figure 4: for exactly the same oxidation test parameters the three dimensional coating keeps on protecting the C/C at 2050°C whereas the two dimensional coating has been totally destroyed. That can be due to an improvement of the bounding of the three dimensional coating because of the SiC whiskers that act like Velcro<sup>®</sup> strips. An oxidation test has been run on the three dimensional coating in which the test temperature has been kept constant at 1900°C. This temperature corresponds to the destruction of the two dimensional coating which occurs for a total test time of 160 s. In the case of the three dimensional coating, the figure 7 shows that this one is destroyed after a total test time of 370 seconds. As a conclusion of the oxidation tests we can say that the three dimensional coating is efficient until 2050 °C and at 1900°C the total time of use is multiplied by two with respect to the two dimensional coating.

### 3.2 C/C protected by sintered coated powder

Figure 8 shows that, after sintering, the coating is dense (95% TD), no cracks can be seen and its thickness is about 300µm. At a higher magnification SiC can be seen at grain boundaries around HfC powder.

In terms of oxidation test on coated powder a TGA until 1500°C under air has been run. Total TGA time is 2h and 30 min. This one is presented on figure 9 where mass gain (%) is presented versus temperature (°C). Oxidation of non coated HfC powder begins at 380°C and is totally finished at 800°C. In reverse SiC is rather stable even at high temperature. The most interesting thing is the fact that the HfC powder coated with 1µm of SiC almost follows the behaviour of pure SiC.



**Figure 8:** SEM micrographs of a coating made of a sintered (SPS) HfC powder coated with SiC over a C/C substrate.



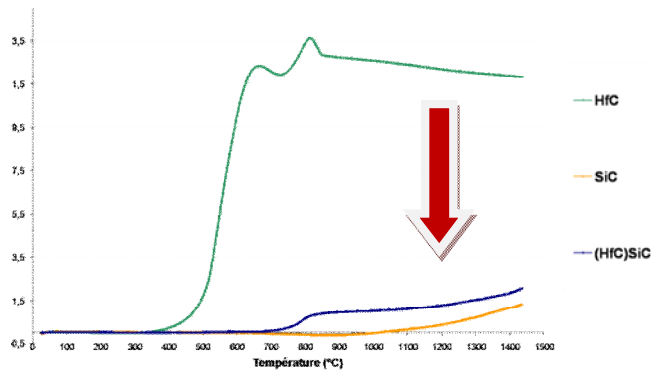


Figure 9: TGA under air until 1500°C of pure HfC, HfC coated with 1µm SiC and pure SiC.

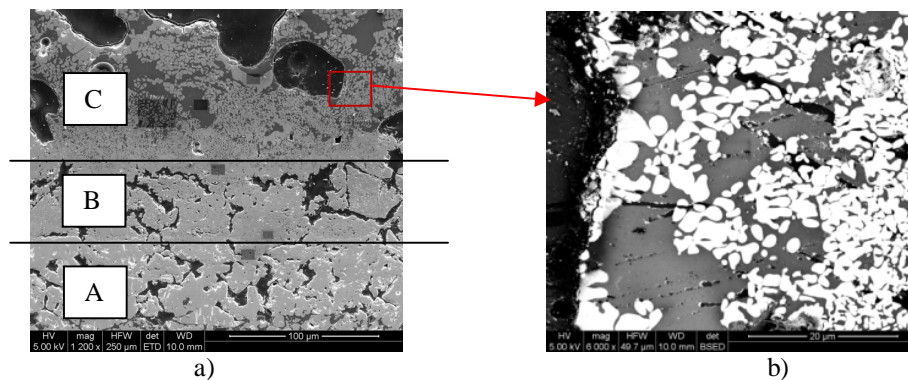


Figure 10: SEM micrographs of a coating made of a SPS sintered HfC powder coated with SiC after oxidation at 2050°C a) BSE. b) BSE.

Figure 10 presents the microstructure of the coating after the oxidation test. This test has been run in an arc image furnace. Maximum temperature reached is 2050°C and time of exposure is 205 seconds [6]. In terms of microstructure after the test, shown in figure 10, it exhibits 3 zones : in zone A the coating is safe it's composed of HfC and SiC with no cracks, in zone B the microstructure is more porous. EDS and electron probe microanalyser analysis have shown that the chemical composition is made of Hf and O in the proportion of HfO<sub>2</sub> without Si. The zone C is more complex. This latter exhibits, at higher magnification in back scattering electrons shown in figure 10 b , two chemical compositions and a microstructure pointing out a melted zone. An EDS analysis, on this C zone, has shown that the darker zone is composed of Si, Hf and O and the lighter zone is composed of Hf and O.

The phase diagram of HfO<sub>2</sub>-SiO<sub>2</sub> shows that at temperatures higher than 1800°C a liquid phase rich in Si can be formed. This liquid phase coexists with HfO<sub>2</sub> at temperatures higher than 1800°C. HfO<sub>2</sub> is solid because its fusion temperature is 2760°C.

So, with respect to the previous observations and to the phase diagram of HfO<sub>2</sub>-SiO<sub>2</sub>, in terms of oxidation mechanisms, HfC and SiC together, give, during oxidation at temperatures higher than 1800°C, a plug of glass rich in Si with particles of HfO<sub>2</sub>, which one protects against O<sub>2</sub> diffusion. This plug of glass and particles is on top of a porous surface of HfO<sub>2</sub>. This oxidation behaviour is explained on figure 11.

Further investigations have to be done to understand the formation of the porous HfO<sub>2</sub> zone (zone B) but we can think that, with respect to the high temperature and to the oxygen partial pressure, the oxidation of SiC is active forming SiO which is a gas. This gas could be responsible of the fact that there is no Si in this zone. Besides, with the increasing of oxygen pressure at the surface, the SiO gas could condense in SiO<sub>2</sub> to form a plug of glass. The oxidation of HfC which gives porous HfO<sub>2</sub> explains the porosities shown in figure 10.

Finally, the liquid phase made up of Si, Hf and O (rich in Si) combined with an HfO<sub>2</sub> structure could be an explanation of the resistance of the HfC/SiC coating against oxidation higher than 1800°C [7].

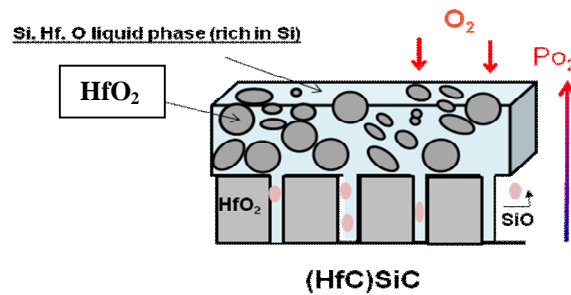


Figure 11: Oxidation behaviour of an HfC/SiC coating over a C/C at temperatures higher than 1800°C.

### Conclusion

Various coatings morphologies synthesized by two CVD techniques have been tested up to 2000°C under air. The two concepts studied have been patented [5, 6]. On one hand the low pressure CVD enables to get thin layers and a final coating of several dozen microns, on the other hand the sintering of a coated powder by fluidized bed CVD enables to get thicker coatings of hundreds microns. Each kind of coatings is dense with no cracks and they all bind the surface of the C/C substrate. Those two kinds of coating are able to protect during several hundred seconds a C/C at a temperature as high as 2000°C.

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