

## Thermo-Mechanical Behaviour Of HfO<sub>2</sub> Coatings For Aerospace Applications

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**Keywords:** Hafnium oxide; Silicon carbide; Oxidization protection; Re-entry tests.

**Abstract.** The use of ceramic composite materials in aerospace applications requires the development of oxidization protection coatings which can withstand very high temperatures. HfO<sub>2</sub> is a promising material as a high temperature oxidization protective layer. HfO<sub>2</sub> coatings have been deposited by radiation frequency magnetron sputtering all over the surface of SiC substrates and were tested under re-entry conditions. Also their oxidization resistance in air in the temperature range 1100 to 1450°C has been examined. The coatings were found to be stable and well-adhering to the substrate even after 100 re-entry cycles. No oxidization of the underlying SiC structure is observed. Re-entry and oxidization tests result in the formation of HfSiO<sub>4</sub> at the HfO<sub>2</sub>/SiC interface, which further promotes their oxidization resistance.

### Introduction

C<sub>f</sub>/SiC and SiC<sub>f</sub>/SiC composite materials (CMCs) and ceramic multilayers with the functionalities of oxidation and abrasion resistance, thermal protection and low friction are candidate materials for space vehicle thermal protection systems, air intake ramps and control surfaces for hypersonic flight vehicles, and moveable aerospace bearing systems [1, 2, 3].

For the application of these bulk ceramics in hostile environments appropriate coatings have to be developed. The very stable HfO<sub>2</sub> is a promising material for a high temperature oxidation protective layer due to its high melting point (above 2900°C) and high transformation temperature to the cubic structure (1700°C) [4]. It is expected that HfO<sub>2</sub> will be relatively un-reactive with water or Na/K-containing atmospheres making it an effective coating material against high temperature oxidation /corrosion. HfO<sub>2</sub> is well known as one of the most important oxide thin-film materials for the interference multilayer coatings in the UV spectral range down to 250 nm [5].

SiC exhibits excellent oxidation resistance at high temperatures, because the formed glassy silica films prevent oxygen diffusion very efficiently and thus serve as protection against further oxidation. However, the amorphous silica at temperatures above 1200°C crystallizes to cristobalite causing surface cracking and also reacts with water or Na/K vapor, resulting in severe degradation of the silica film [6].

Based on these assumptions, the combination of HfO<sub>2</sub> and SiC should result in an excellent oxidation resistant material. Purpose of this work is to test the thermo-mechanical behavior of HfO<sub>2</sub> coatings at elevated temperatures, and the degree on which HfO<sub>2</sub> film can act as a protection layer to oxidation of the underlying structure, as well as, to suggest approaches to improve the desired functionalities of the oxide film.

## Experimental

Coatings of  $\text{HfO}_2$ , having a nominal thickness of 7  $\mu\text{m}$ , were deposited using a Cooke CVE401 radio-frequency (rf) magnetron sputtering system on a sintered SiC substrate (The Technical Glass Company). A 2"-diameter hot-pressed  $\text{HfO}_2$  target of 99.95% purity was used. The sputtering chamber was evacuated to a base pressure of  $1 \times 10^{-7}$  Torr and the target–substrate distance was 5 cm. The deposition temperature, the argon pressure and the flow rate were 70°C, 30 mTorr and 60 sccm, respectively. Depositions were performed with an rf power of 200 W, resulting in a deposition rate of 3.9 Å/s. The SiC substrates were disks having 10 mm diameter and 1 mm thickness. The whole SiC surface was covered by the deposited  $\text{HfO}_2$ .

For the oxidization resistance tests a tubular furnace open in ambient air was used. The samples were treated in the temperature range from 1100 to 1450°C for one hour.

Tests of the  $\text{HfO}_2$  coatings under re-entry conditions were carried out in ARC's re-entry test rig at a maximum temperature of 1450°C for up to 100 cycles. The thermal test profiles as presented in Fig. 1 have been taken from the HOPPER study and were already employed for the ESA project "OLCHOS" [7, 8, 9]. Contrary to Ref. [7, 8, 9], the tests were performed under an air pressure profile representative for an atmospheric re-entry rather than at a constant pressure.

X-Ray diffraction and scanning electron microscopy measurements were used for the post examination of the samples in order to assess the degradation mechanisms and the degree of oxidation of the substrate.

The X-ray diffraction (XRD) and grazing incidence diffraction (GID) measurements were performed at a D8 Bruker system using Cu Ka radiation. For the scanning electron microscopy (SEM) measurements a Quanta Inspect system coupled with energy dispersive X-ray spectroscopy (EDS) was used.

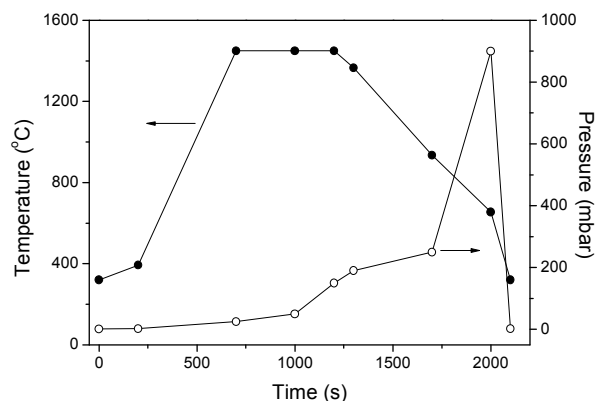


Fig.1. Thermal and pressure profiles of the re-entry tests.

## Results and Discussion

The as-fabricated  $\text{HfO}_2$  coatings were found to crystallize in the monoclinic system P21/c (Fig.2). After oxidization in the temperature range 1100 to 1450°C re-crystallization of  $\text{HfO}_2$  takes place which results in grain growth. This can be observed in the diffraction spectra presented in Fig.2 as a decrease in the width of the  $\text{HfO}_2$  Bragg peaks. Oxidization at 1450°C results in the formation of  $\text{HfSiO}_4$  (Fig.2), which enhances the good bonding of the layer with the underlying SiC substrate and further increases the oxidization resistance of the coating. In addition, at this temperature, a very small amount of  $\text{SiO}_2$ , in the form of cristobalite, has been detected (Fig.2). This could be explained by an initial formation of amorphous silica which then transforms to cristobalite above 1200°C [5].

The  $\text{HfO}_2$  coatings were subjected to re-entry tests up to 100 cycles at 1450°C. These tests showed no flaking-off of the coatings. After an initial mass loss, mass gain is observed. However,

SEM examination of the surface (Figs. 3 and 4) showed that platinum crystallites, arising from Pt evaporated from the susceptor tube of the induction heater, had been deposited on the surface of  $\text{HfO}_2$ . This has also been confirmed by XRD and GID measurements. The Pt mass deposition was estimated to be of the order of the mass gain monitored during the re-entry test cycles and thus, the mass gain/loss curves versus the number of cycles can not be quantified.

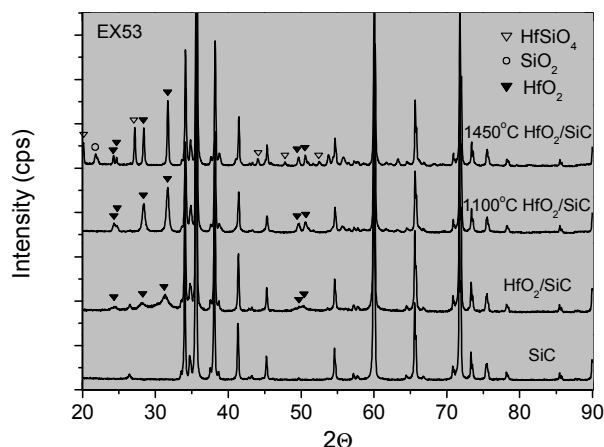


Fig.2. X-ray diffraction spectra of the as-fabricated  $\text{HfO}_2$  coatings on SiC and after oxidization in air at 1100 and 1450°C. Bottom spectrum refers to the SiC substrate. Triangles:  $\text{HfO}_2$  (solid) and  $\text{HfSiO}_4$  (open) Bragg peaks. Open circle:  $\text{SiO}_2$  Bragg peak.

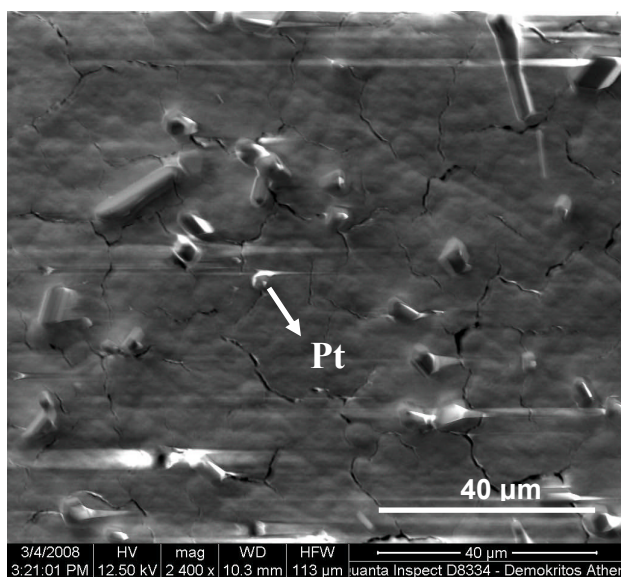


Fig. 3. SEM view of the surface of the  $\text{HfO}_2$  coatings after 50 re-entry cycles at 1450°C. The arrow shows the Pt crystallites.

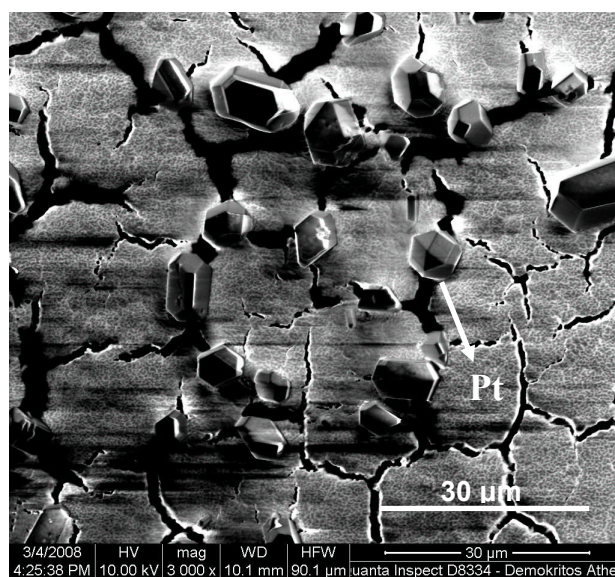


Fig. 4. SEM view of the surface of the  $\text{HfO}_2$  coatings after 100 re-entry cycles at 1450°C. The arrow shows the Pt crystallites.

The XRD spectra showed no change of the crystallographic structure of the  $\text{HfO}_2$  coatings after the re-entry tests and, as in the case of oxidation in air, grain growth is observed. From GID measurements it was found that  $\text{HfSiO}_4$  is formed after both 50 or 100 re-entry cycles (Fig. 5). This phase could not be detected by normal XRD measurements, indicating that the amount of  $\text{HfSiO}_4$  after the re-entry tests is lower than that formed under the oxidization tests. The cristobalite phase of  $\text{SiO}_2$  was not detected. As both temperature and oxygen partial pressure are instationary during the

re-entry tests, the oxidation kinetics and the reaction products formed may be different to those of isothermal oxidation tests.

The surface examination of the coatings by SEM showed the formation of cracks (Figs. 3, 4) which is due to the re-crystallization process and at least partly due to the thermal mismatch between coating and bulk material. The crack size increases with the number of re-entry cycles and is in the range of about 1 to 3  $\mu\text{m}$ . EDS analysis shows that the cracks are filled with  $\text{SiO}_2$ . Thus, their formation is by no means detrimental to the functionality of the coatings under the conditions tested.

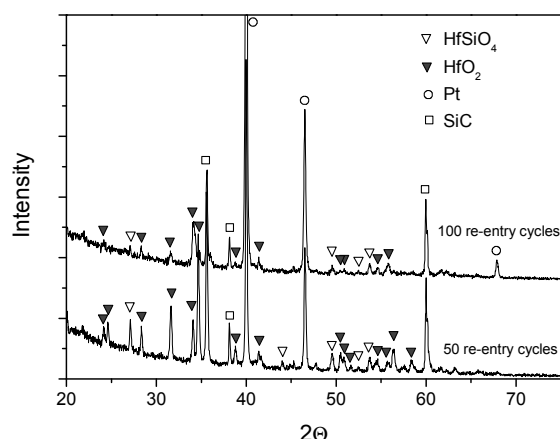


Fig.5. Grazing incidence X-ray diffraction spectra of the  $\text{HfO}_2$  coatings on SiC after 50 and 100 re-entry cycles at  $1450^\circ\text{C}$ . Triangles:  $\text{HfSiO}_4$  (open) and  $\text{HfO}_2$  (solid) Bragg peaks. Open circles: Pt Bragg peaks. Tetragonal: SiC Bragg peak.

The SEM view of the cross-sections of the  $\text{HfO}_2$  coatings after 50 re-entry cycles is presented in Fig. 6. The dark areas in the SiC substrate are the pores of the sintered SiC substrate. The  $\text{HfO}_2$  layer follows the roughness of the substrate surface and remains adherent to it. The element analysis through the cross-section of the  $\text{HfO}_2$ /SiC interface is depicted in Fig. 7. At the  $\text{HfO}_2$ /SiC interface and in thickness of around 1  $\mu\text{m}$  the element analysis (Fig. 7) is consistent with the  $\text{HfSiO}_4$  phase observed by GID measurements. Possibly a percentage of this phase is amorphous, as it has not been detected by normal XRD. Some formation of  $\text{SiO}_2$  can not be excluded. The important finding is that no oxidization of the SiC substrate, even after 100 re-entry cycles, is observed.

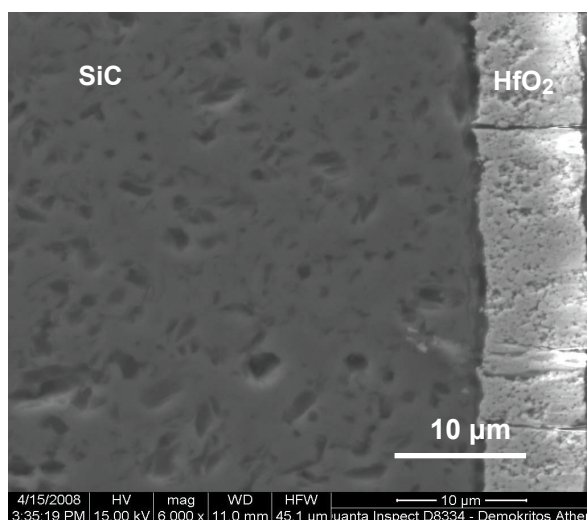


Fig. 6. SEM view of the  $\text{HfO}_2$ /SiC cross-section after 50 re-entry cycles at  $1450^\circ\text{C}$ .

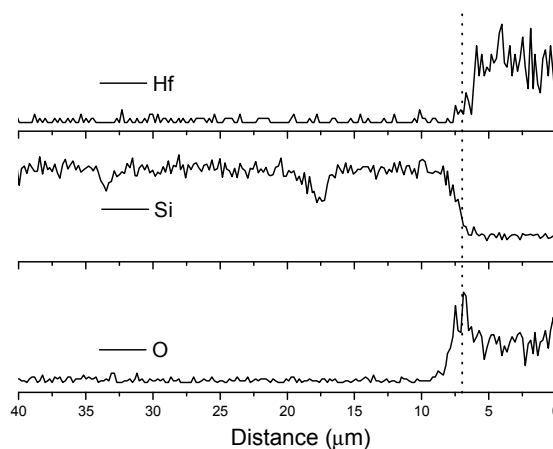


Fig. 7. Line scan across the cross-section after 50 re-entry cycles at  $1450^\circ\text{C}$ , showing O, Si and Hf variation versus distance from the free surface. The dotted line indicates the  $\text{HfO}_2$ /SiC interface.

## Conclusions

This study has shown that the HfO<sub>2</sub> coatings deposited by rf magnetron sputtering on SiC substrates prove to be very promising high temperature oxidization resistant coatings and effectively protect the underlying structure in re-entry conditions. The coatings remain intact even after 100 re-entry cycles at 1450°C and no oxidization of the underlying SiC layer is observed. Application on other substrates is under investigation, and preliminary results are very promising.

## Acknowledgement

This work has been carried out within the framework of the Integrated European Project “ExtreMat” (contract NMP-CT-2004-500253) with financial support by the European Community. This paper only reflects the views of the authors and the European Community is not liable for any use of the information contained therein.

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