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Hafnium and silicon carbide multilayer coatings for the protection of carbon composites

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ABSTRACT

A solution to protect the surface of a carbon/carbon composite from oxidation at high temperature is to combine refractory carbides, such as hafnium and silicon carbides (HfC and SiC). Their depositions have been studied on flat substrates and present major protection against oxidation at high temperature (several minutes at 2000 °C under air). The infiltration of these carbides layers has been observed inside the open porosities of the carbon substrate which enhance the adhesion of the protection.
The low pressure chemical vapor deposition (LPCVD) process developed here allows multilayer HfC/SiC depositions. The HfC coatings have various morphologies and thicknesses depending on the experimental conditions (temperature, pressure, dilution). This carbide has been firstly deposited over flat graphite substrates and carbon single fibers. Secondly, the multilayer coating deposition over a C/C composite and over carbon single fibersis studied. Finally, HfC layers have been infiltrated inside carbon fiber tows. To avoid the notch effect on the carbon fibers, a thin layer of pyrocarbon (50 nm thick) has been deposited prior to the growth of the carbides. All the coatings were done in a hot wall CVD reactor and their morphologies and chemical compositions characterized by scanning electron microscopy.

1. Introduction

Composites can combine lightness and high thermo-mechanical properties to be used as structural components. C/C composites (carbon fibers embedded into a carbon matrix) are especially well-suited since they keep high toughness, shear and stress strength at very high temperatures. However, these composites have a major drawback, they exhibit a poor lifetime under an oxidizing atmosphere; carbon starts to be oxidized under air at a temperature of 400 °C [1]. To protect these composites from oxidation, many coatings made of Ultra High Temperature Ceramics (UHTCs) have been tested [2,3] such as TiB_2, ZrB_2… They can be synthesized by many ways: CVD with halogeneous [4] or metal-organic precursors [5], or reactive melt infiltration [6] for example.

In a previous work, two refractory carbides have been selected and deposited on flat substrates, SiC and HfC that develop a synergetic effect against oxidation [7]. A multilayer HfC/SiC coating that allows a good oxidation resistance has been obtained [7–9]. The coatings consist of five or ten alternated layers of SiC and HfC with a total thickness of 20 or 40 μm. The aim of this study is to investigate the infiltration of this multilayer coating in a C/C composite. The SiC deposition and infiltration are well known and industrially applied. However, the difficulty of the HfC/SiC multilayer coating deposition is due to the HfC layer itself. Consequently, this study was focused on the HfC deposition and in particular on infiltration parameters (such as temperature, duration) and their influences on the morphology and thickness of the coatings.

First of all in this paper, the low pressure chemical vapor deposition (LPCVD) equipment is described. Secondly, the growth rate of HfC and the microstructure variation versus temperature is exposed on flat graphite substrates and carbon single fibers. Then, the first results of multilayer deposition on flat graphite substrates and carbon single fibers are presented. Finally, the multilayer coating infiltration results within more and more porous substrates, PyC/HfC/SiC in C/C composites with some large open pores and then PyC/HfC inside carbon fiber tows, are exposed. The pyrocarbon (PyC) layer was deposited prior to the multilayer coating on the carbon single fibers to disconnect the carbon fiber from the brittle carbides. It reduces the notch effect which can occur between a carbon fiber and brittle carbides.

2. Experimental procedure

2.1. Deposition equipment

The multilayer coatings were prepared by LPCVD by using three interconnected devices (Fig. 1).

The first one was a chlorination device in which $HCl_{(g)}$ reacts with metallic $Hf_{(s)}$at 700 °C to form $HfCl_{4(g)}$, the main gaseous precursors of Hf. The HfC precursors were $CH_{4(g)}$, $HfCl_{4(g)}$and$H_{2(g)}$. $HfCl_{4(g)}$ precursor

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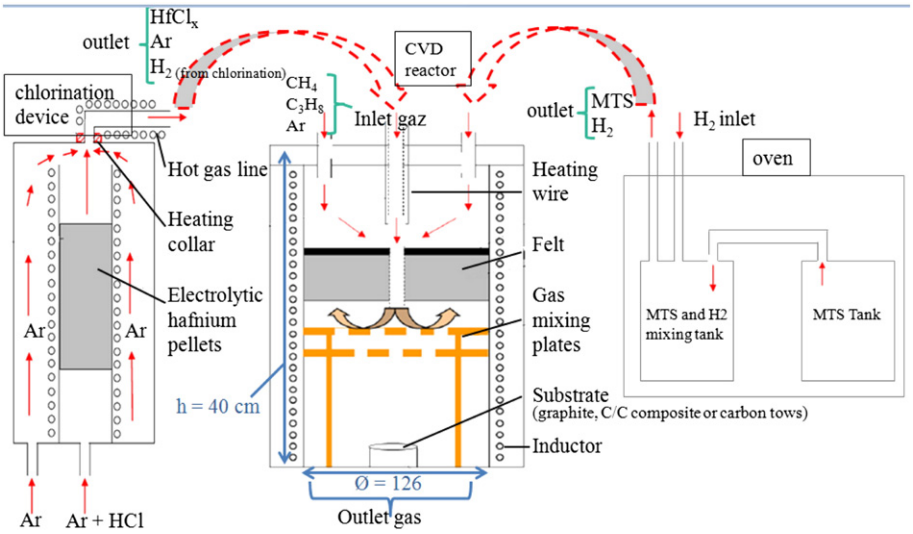

Fig. 1. Reactor and chlorination device diagram with involved gases flows and precursors.

was injected with argon as a carrier gas (flow rate of 350 sccm) into the second device through a pipe heated at 500 °C to avoid its condensation. Throughout the study the $H_2/HfCl_4$ ratio was 7.5 with flow rates of 750 sccm for $H_{2(g)}$ and 100 sccm for $HfCl_{4(g)}$.

This second device was the hot-wall CVD reactor itself which contained the substrates and where both carbide layers, HfC and SiC, and PyC were deposited at a temperature ranging from 900 to 1100 °C. The SiC layers were classically deposited from methyltrichlorosilane (MTS) and hydrogen with a H_2/MTS ratio of 4. The third device was an oven containing the MTS and allowing its evaporation and its dilution in hydrogen. PyC layers were deposited from $C_3H_{8(g)}$, with a flow rate of 200 sccm, directly injected inside the CVD reactor.

Throughout the study, HfC and SiC layers were deposited at 5 kPa, and the PyC layers at 2 kPa on carbon single fibers or in fiber tows, whereas a total pressure of 15 kPa was used for the carbide deposition on flat graphite substratesor C/C composites.

2.2. Substrates and reagents

The C/C composites (density > 1.90) were proprietary materials. Fiber substrates were either T300 carbon single fibers (diameter of 7 μm) or dry 3 k T300 carbon fibers tows (Toray, Japan), i.e. matrix-free multifiber tows (for infiltration runs), both types being pretreated under vacuum at 800 °C to thermally remove the sizing. The hafnium metal was an electrolytic grade $Hf_{(s)}$ supplied by Areva. The MTS was supplied by Sigma Aldrich and its purity was superior to 97%.

2.3. kinetic study and morphology

The HfC deposition kinetics was studied first by measuring the thickness of HfC layers deposited on the flat graphite substrates for 2 h at a temperature ranging from 950 to 1050 °C and then on carbon single fibers at 1020 °C for durations ranging from 25 to 60 min. In the last case, the studied coatings consisted of a stack of two dual-layers PyC/HfC referred to as $(PyC/HfC)_2$, i.e. a PyC/HfC/PyC/HfC multilayer sequence. The first PyC layer was used as a mechanical fuse to prevent the weakening of the fibers due to the thermal expansion mismatch and to reduce the notch effect which can occur between a carbon fiber and brittle carbides. The second PyC layer was used to distinguish the first layer of HfC to the second one deposited during the same experiment.

For the morphology study, the $(PyC/HfC)_2$ multilayer coatings were deposited at temperatures ranging from 900 to 1100 °C and compared. The second part of the HfC kinetic deposition study has been realized on fibers within the scope of further coating infiltration. This study has been done at a lower pressure (5 kPa instead of 15 kPa) because a lower pressure improves coating infiltration in porous media [10,11]. The $(PyC/HfC)_2$ multilayer coatings were also infiltrated inside carbon fiber tows at 950 °C and 1100 °C.

2.4. Characterizations

The coating morphologies were observed by scanning electron microscopy (SEM, Hitachi S4500 FEG) with a secondary electron (SE) detector and an accelerating voltage fixed at 10 kV. A second SEM microscope (Quanta 400 FEG V2 microscope) with an accelerating voltage fixed at 5 kV was also used for the coating observations and layer thickness measurements. This last SEM is equipped with a Back Scattering Electrons detector (BSE) which completes the secondary electron analysis.

The crystal structure of the sample surface was studied by X-ray diffraction (XRD) with a Diffractometer D8 advance Bruker (CuKα).

3. Results and discussions

3.1. HfC deposition by LPCVD on flat graphite substrates and carbon single fibers

Fig. 2 shows the thickness variation versus temperature of HfC coatings deposited on flat substrates. This graph reveals that HfC coating deposition is highly thermally activated.

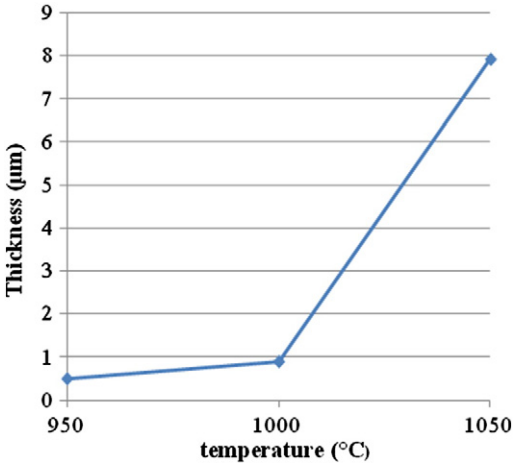

Fig. 2. HfC thickness evolution versus temperature P = 15kPa, deposition time: 2 h.