

PROTECTIVE CERAMIC MULTILAYER COATINGS FOR CARBON MATERIALS

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Introduction

For aeronautic and aerospace applications, a conventional way to protect carbon fibres against oxidation can be achieved with a ceramic coating obtained by a chemical vapour infiltration process [1-3]. This technology cannot be transferred to the carbon fibres used as heating elements, because of the complexity and the cost of this process. Therefore, there is a need to develop other oxidation protection routes. The possibility to obtain a silicon carbide or a mixed carbide layer by a replica technique starting from carbon fibres as template was shown in previous works [4-6]. The process can be summarized as follows: PAN-based carbon fibres are covered with an oxide layer obtained by a sol-gel process. By heat treatment in a inert atmosphere at temperatures higher than 1000°C, the carbon reacts with the oxide leading to the formation of a carbide interphase. A hollow tube of carbide (e.g. SiC, TiC) or mixed carbides (e.g. SiC-TiC) can be obtained after removal of the unreacted carbon and silica by selective treatments; this method keeps the morphology of the initial carbon fibres. This reactive templating process was successfully applied to obtain a carbide woven replica from a carbon cloth (2D carbon fibres) as shown in Figure 1. By this means, layers or multi-layers of either one type of carbide or a mixture of carbides were formed on the carbon surface. The protective efficiency of the ceramic coating was tested in air between 500 and 800°C. This temperature range corresponds to the working temperature of these materials. The objective of this work is to study the behavior in air of the prepared carbon/carbide(s) materials. It will be shown that this behavior is depending on parameters such as the conditions of preparation of the carbide(s), the composition and chemical nature of the carbide layers as well as the type of carbon woven used.

Experimental

Two types of carbon woven were used : a rayon-based carbon cloth supplied by Messier-Bugatti and heat-treated at 1600°C (named A in the text) and a commercial polyacrylonitrile-based carbon cloth (M40) (noted B). The carbon cloth was covered by the oxide corresponding to the desired ceramic (e.g.: SiO₂ for SiC, TiO₂ for TiC, HfO₂ for HfC). The mixed carbide SiC-TiC was obtained from a mixed oxide prepared by a sol-gel technique [6]. The sols of the different oxides and mixed oxides were prepared according to the procedures described in the literature [4-7].

Tetraethoxysilane, tetrabutoxyde titanium and hafnium tetra-chloride were selected as SiO_2 , TiO_2 and HfO_2 precursors, respectively. The covering process is described elsewhere [5]. The as-prepared C/oxide(s) samples were placed in an alumina reactor in a way to avoid any contact between the sample and the reactor. Argon at atmospheric pressure with a linear flow rate of 20 L/h was introduced into the reactor. The reactor was heated up to 1000°C with a linear heating rate of 300°C/h and from 1000°C to the final carbothermal temperature at 120°C/h. The final carbothermal reaction temperature as well as the duration of the plateau are depending upon the chemical nature of the carbide(s). The experimental conditions for the formation of carbide(s) were adjusted so that the degree of conversion of the oxide into carbide is equal to 1. The heat-treated samples were recovered and characterized after cooling down in argon. The as-obtained carbon/carbide(s) materials were subsequently oxidized in air at atmospheric pressure at 600°C and the kinetics of carbon oxidation was followed by thermogravimetric analysis. After removal of the remaining carbon by oxidation, the solid was characterized by X-ray diffraction, gas adsorption at 77K and scanning electron microscopy.

Results and Discussion

Several carbon/carbide(s) materials were prepared and tested in air. Their preparation conditions are summarized in Table 1. The oxides were converted into the corresponding carbides at the temperatures corresponding to the highest values indicated in the table. The mechanisms of conversion depend on the nature of the carbides. For example, the formation of SiC occurs via a gaseous intermediate (SiO) whereas for TiC, intermediate solid-solid reactions take place. The morphology of the coatings are observed by SEM after removal of the unreacted carbon (Figure 2). The coating appears homogeneous whatever the chemical nature of the carbides.

Materials	Type of carbon fibres	Oxide(s) prepared by sol-gel	Carbide(s) formed	Conditions of heat treatment	Thickness (μm)	I_f
A/HfC	A	HfO_2	HfC	8h at 1000 °C and 8h at 1900 °C	< 0,1	2
A/HfC/SiC	A	HfO_2 then SiO_2	HfC/SiC	8h at 1000 °C and 8h at 1900 °C	0,1	4
A/SiC/HfC	A	SiO_2 then HfO_2	SiC/HfC	8h at 1000 °C and 4h at 1450 °C (for SiC) and 8h at 1900 °C (for HfC)	0,35	4
A/SiC or A + SiC	A	SiO_2	SiC	8h at 1000 °C and 8h at 1450 °C	0,15	2,5
A/SiC/SiC	A	SiO_2	SiC/SiC	8h at 1000 °C and 8h at 1450 °C	0,5	8,3

A/SiC/SiC/SiC	A	SiO ₂	SiC/SiC/SiC	8h at 1000 °C and 8h at 1450 °C	0,3	2
A/TiC-SiC/SiC	A	TiO ₂ -SiO ₂ then SiO ₂	TiC-SiC/SiC	8h at 1000 °C and 8h at 1450 °C	between 0,15 and 0,3	8
B + SiC	B	SiO ₂	SiC	8h at 1000 °C and 8h at 1450 °C	0,1	11

Table 1: Experimental parameters for the preparation of the C/Carbide(s) materials

The materials noted C/carbide/carbide (e.g. C/SiC/SiC) and C/mixed carbides (e.g. C/SiC-TiC) were prepared according to the procedure summarized in Figure 3.

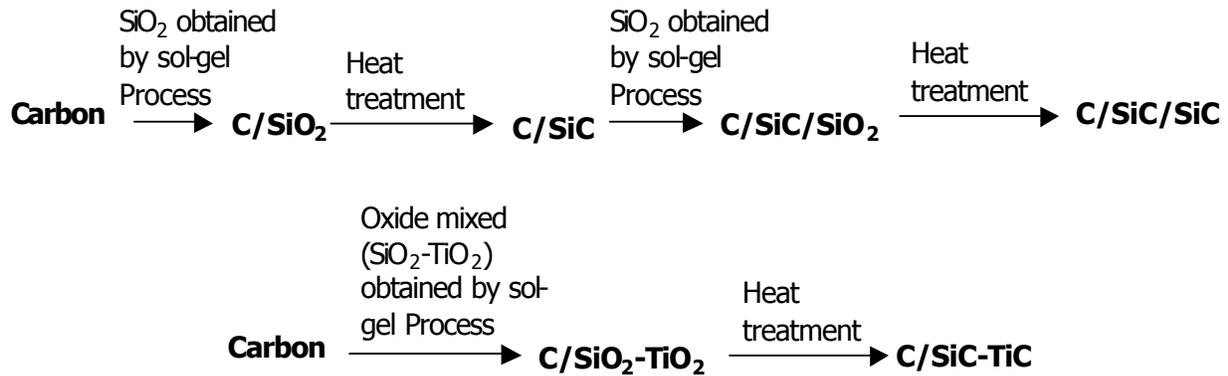


Figure 3. Schematical representation of the synthesis process for the obtention of C/SiC/SiC and C/SiC-TiC (carbide mixed) materials (the experimental conditions are indicated in table 1)

The thickness of the carbide layer was estimated from SEM observations. This value depends on the sol which was used (nature and preparation conditions). The lowest value is obtained with the HfC coating, the highest one with the SiC/SiC coating. The oxidation resistance of the different carbon/carbide(s) materials prepared with carbon A is illustrated on Figure 4 representing the variation of the weight loss of the carbon component during the oxidation. In order to evaluate the efficiency of the protection, an inhibitor factor I_f was defined as the ratio of the oxidation rate at 50% of burn-off for the uncoated carbon to the rate corresponding to the carbon with a ceramic coating. The values of I_f are reported in Table 1. The most efficient protective coating is the double layer of SiC. The oxidation curves as well as the values in Table 1 indicate that several parameters influence the protective efficiency : the thickness of the coating, its chemical nature, the carbon/coating interface, the texture of the coating (porosity, crack...). The multi-layer coating corresponding to a layer of mixed carbide (SiC-TiC) and a layer of SiC are efficient for an oxidation time lower than 6 hours. Some experimental conditions

of preparation of the SiC double-layer coating appears in table 1. The SiC obtained at a low carbothermal temperature is more efficient than the same material prepared at 1900°C. When an additional SiC layer is added on the C/SiC/SiC material, the protective efficiency decreases (see Figure 5) as well as the thickness of the coating (see Table 1). This may be explained by the fact that the gaseous intermediate SiO(g) resulting from the reaction between the SiC layer and deposited SiO₂ layer cannot reach the carbon by diffusion to react further with it and form SiC. In this case, the SiO diffuses out of the sample and is converted into SiO₂ in the cooler part of the furnace.

In such composites, the nature of the carbon/carbide interface plays an important role. This interface can be modified by using other carbon fibres. The oxidation behavior of a C/SiC/SiC material obtained from carbon fibres A and B is represented in Figure 6. As indicated by the I_f values, the protection is much more effective when the SiC coating is deposited on carbon B.

Conclusion

The formation of a ceramic layer with a controlled morphology was obtained by a replica reactive process using different oxides (TiO₂, SiO₂, HfO₂...) and mixed oxides (SiO₂-TiO₂). The protective efficiency of the ceramic coatings against carbon oxidation was studied. The following parameters influence the protection of carbon against oxidation : (a) the thickness of the protective coating, (b) the carbon/oxide (ceramic) interface partly controlled by the surface characteristics of the carbon fibres , (c) the nature of the oxide (d) the mechanism of formation of the carbide.

Acknowledgment

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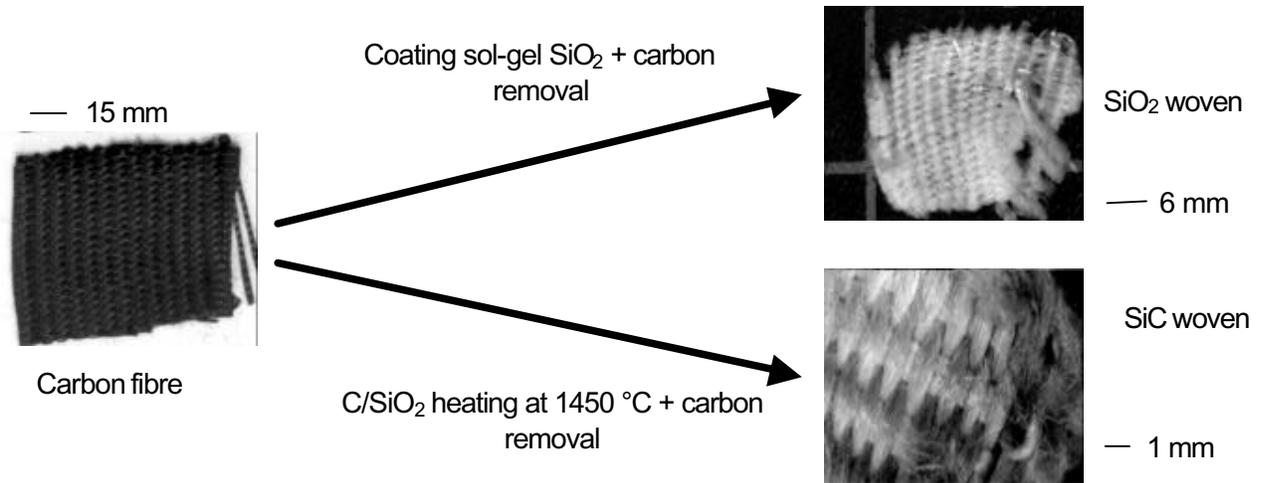


Figure 1. The reactive templating process to obtain a carbide or oxide woven replica from a carbon cloth

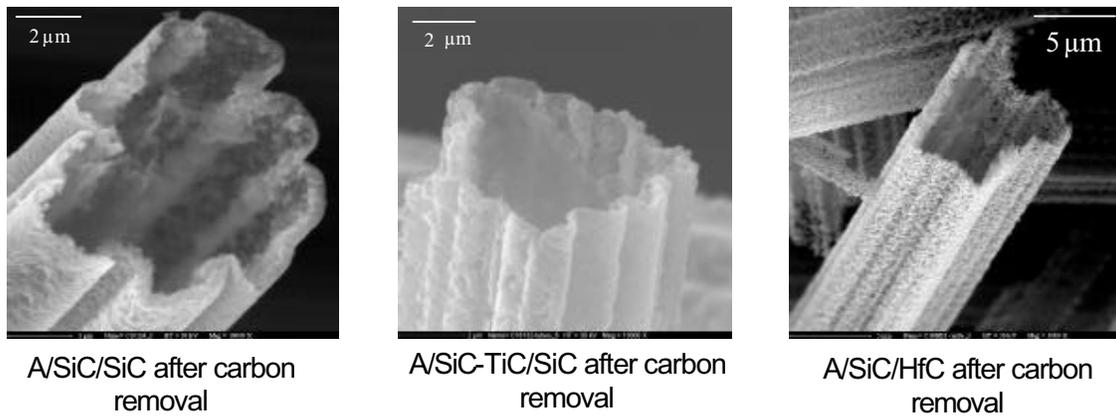


Figure 2. SEM images of the SiC/SiC, SiC-TiC/SiC and SiC/HfC tubes

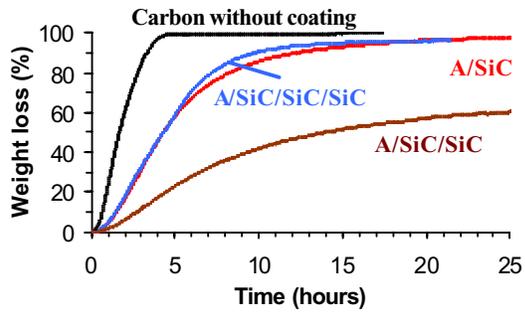


Figure 4. Evolution of the weight loss of the carbon coated with carbides, as a function of time during oxidation at 600°C in air

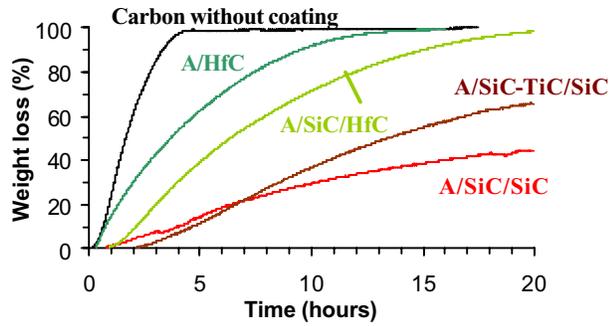


Figure 5. Evolution of the weight loss of the carbon coated with one or multiplayer(s) SiC, as a function of time during oxidation at 600°C in air

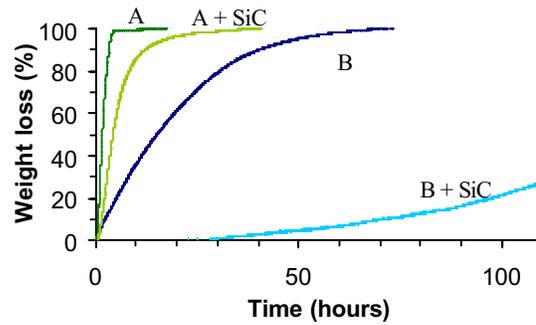


Figure 6. Evolution of the weight loss of the sample A and B coated with SiC, as a function of time during oxidation at 600°C in air