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Abstract. — Based on their good mechanical properties, potential uses of structural carbon materials have been identified for future manned hypersonic vehicles and other aircraft applications. Carbon based composites are expected to be used for periods ranging from a few hours (at high temperature) to a few thousands of hours (at low temperature) in oxidizing environments. Unfortunately carbon reacts rapidly with oxygen at temperature as low as 500 °C. Therefore numerous researches have been conducted in an attempt to protect carbon-carbon composites against oxidation. The protection mechanism relies on different concepts depending on the temperature range. Two different basic approaches have been considered to protect carbonaceous materials: 1) a microscopic one (at low temperature) using poisoning agents which adsorb on the active sites responsible for the carbon gasification; and 2) a macroscopic one (at high temperature) using an oxygen barrier. Hence the difference in thermal behavior that exists between this layer and the carbon substrate results in coating cracks. Therefore other approaches have been developed including: a) transition layer; b) inhibited matrix; c) coating on fibers. Temperature, pressure and oxidizing atmospheres limitations of all these concepts are discussed. Typically, protection for extended periods can be achieved in a limited range of pressure and temperature by the use of several concepts and multilayer coating.

1. Introduction.

Structural carbon materials in the form of carbon fiber-reinforced carbon matrix or carbon-carbon composites are gaining increasing importance because of their high toughness, high strength and low weight. In a non oxidizing environment, carbon fibers retain their modulus, strength and their high mechanical properties to high temperatures. Based on their good mechanical performances, potential uses of structural carbon materials have been identified in future manned hypersonic vehicles (Hermes, Sänger, Hotol) and in other aircraft applications. However most of these applications involve extended time periods in oxidizing atmospheres. Unfortunately, carbon-carbon composites react rapidly with oxygen at temperatures as low as 500 °C and are subject to oxidation degradation. Therefore, numerous researches have been conducted in an attempt to protect carbon based composites against oxidation.

The protection mechanism relies on different concepts depending on the temperature range. Two different basic approaches have been considered to protect carbonaceous materials:

1) a microscopic one (at low temperature) with the use of poisoning agents which adsorb on the active sites responsible for the carbon oxidation gasification;

2) a macroscopic one with the use of a barrier against oxygen diffusion at high temperature.

(*) Keynote lecture.
Due to the desorption of adsorbed poisoning agents and the increase of the number of active sites, the first concept cannot be used above 900 °C.

The main problem, when applying the second concept, is the thermal mismatch between coating and carbon substrate which results in cracking of the coating. Therefore other approaches have been developed including:

1) intermediate layer;
2) inhibited matrix;
3) fiber protection.

The purpose of this work is to evaluate the inherent limitations of the various approaches being considered and to summarize most of published work being realized.

For this discussion, we assume that good mechanical properties are preserved for a mass loss below 3%, and we define short, middle and long-term applications according to the time (15 minutes, 15 hours and 100 hours respectively) needed to reach this mass loss.

2. Protection by active sites poisoning.

Crystalline graphite may be considered as a model compound for the carbon-carbon composites. In a graphite lattice (Fig. 1) edge atoms are more reactive than basal atoms and are the main active sites. On the edge of layer planes, two types of active sites are present: zig-zag sites (with alternate labile carbon atoms) and arm-chair sites (with adjacent labile carbon atoms) (Fig. 1). Others active sites may exist including point defects and screw dislocations. Below 900 °C, gasification from molecular oxygen attack on carbon is dominated by the oxidation of zig-zag sites [1]. Therefore, adsorption of poisoning agents on these sites should inhibit the reaction.

Fig. 1. — Graphite crystal lattice.
Three types of poisoning agents (or active site passivators) have been studied: halogens, boron compounds and phosphorus compounds. Pretreatment with liquid organohalogen compounds is not effective [2], due to their desorption from the carbon surface at temperatures as low as 100-300 °C. The pretreatment with gaseous chlorine is more effective, but halogen atoms are desorbed about above 900 °C [2-6]. Bromination [7-9] was found to increase the oxidation resistance of poorly graphitized carbon fibers but caused physical damage in more graphitic fibers by decreasing their oxidation resistance. Stronger poisoning effects were observed with phosphorus compounds [10-12] or organo-borates and boron oxide [13, 14] which adsorbed on “zig-zag” sites. But these adsorbed radicals also enhanced adsorption of water, and therefore, this type of protection is effective only in dry atmosphere. Some silicious compounds have been tested [15, 16], but a complete blockage of the active sites is not achieved due to the large size of the molecules [15].

Experimental published results indicate that the maximum temperatures up to which poisoning agents are effective are 600 °C and 750 °C for middle and short-term dry applications respectively.

At higher temperatures, this protection concept is no more valid due to the increase of the diversity of active sites and reactional mechanisms. Theoretical calculations, carried out by Luthra [72], indicated that maximum temperatures, which could be reached with stronger poisoning agents, are 600 °C and 900 °C for middle and short-term applications. Therefore, for higher temperatures, the concept of oxidation protection by coating has been developed.

3. Coatings.

3.1 Oxygen barrier layer. — Desired properties for the coatings on carbon-carbon composites are thermal expansion compatibility (Fig. 2) to minimize cracks, low oxygen and carbon diffusion, low vapor pressure, chemical compatibility with carbon, erosion, wear and impact resistance.

The main coatings studied are based on noble metals, phosphates, boron, oxides, carbides, silicides.

3.1.1 Noble metals. — Refractory group metals, such as iridium and ruthenium, are potential elements for oxidation protection systems of carbon-carbon [16, 18]. Iridium has a high melting point (2447 °C), a very low oxygen permeability and is chemically compatible with carbon (formation of an eutectic at 2110 °C, no carbide formation). However, its high thermal expansion coefficient (TEC), poor adherence to carbon materials, erosion via volatile oxidation, high cost and short supply limit its use [18-21]. At the present time, iridium is used in multilayer coating concept [22] (Chap. 5).

3.1.2 Phosphate coatings. — Many phosphate coatings have been studied for the oxidation protection systems. They include aluminium [23], magnesium [23], ternary compounds [24], alkali and alkaline metals [25]. They are usually either mixed with ceramic powders [25] or applied on a transition layer such as SiC [23]. But they can only be used at low temperatures (up to 850 °C) in a dry atmosphere for short-term applications.

3.1.3 Boron-based coatings. — Boron oxide is an attractive compound for the protection against oxidation. The chemical compatibility of B₂O₃ with carbon, its good wetting property and its low viscosity (10⁴ to 10² dPa in the 600-1100 °C range) allow the formation of thin protective glass films [19, 26-28]. Under dry conditions, borate glass coatings can be used up to 600 °C and 1000 °C for long and short-term applications respectively [19, 72].
Fig. 2. — Percent thermal expansion as a function of temperature for some ceramic materials and carbon fibers according [48].

The main limitations of borate glasses are their moisture sensitivity [29] (hydrolysis under ambiant conditions) and at higher temperatures the vaporisation of boron oxide [26].

3.1.4 Oxides. — Oxides have numerous advantages but generally they have too large thermal expansion coefficient (TEC) [19, 20, 30-33]. Therefore, it is very difficult to apply crack-free coatings. Other limitations are due to:

- fast oxygen diffusion through oxides phase (for instance ZrO₂, HfO₂ have high oxygen permeability);
- oxide reduction by the carbon (as low as 1200 °C for silica, 1730 °C for ZrO₂, 1750 °C for HfO₂).
- total gas pressure at the oxide-carbon interface causing spallation (1 atmosphere at 1500 °C for the silica/carbon system).

Therefore direct oxide deposit on carbon must be avoided. Oxide are generally used as the upper layer (oxygen barrier layer) in multilayer coatings.
3.1.5 Silicides. — Molybdenum disilicide coatings have been used for the oxidation protection [34] but these compounds react with carbon and have a high TEC. Therefore an intermediate layer to isolate them from carbon is needed.

3.1.6 Silicon carbide and silicon nitride. — Silicon carbide and silicon nitride are the best candidates for the oxidation protection of carbon. The thermal expansion coefficient (TEC) of these compounds and of silica is near the TEC of the carbon-carbon composites (Fig. 2). In spite of this good adequation, it is difficult to form coatings without cracks. Therefore at low temperatures, \((T < 1250 \, ^\circ\text{C})\) (domain I, Figs. 3 and 4), it works only for short-term application [39]. At higher temperatures (domain II, Figs. 3 and 4) due to the formation of low viscosity silica, it works for middle-term application. At very high temperatures or middle temperatures and low oxygen pressures (domain III, Figs. 3 and 4), silica does not protect.
anymore because of the formation of gaseous silicon monoxide by [40-52]:
• active oxidation

\[
\begin{align*}
\text{SiC} + \text{O}_2 & \rightarrow \text{SiO} + \text{CO} \\
\text{Si}_3\text{N}_4 + \frac{3}{2} \text{O}_2 & \rightarrow 3 \text{SiO} + 2 \text{N}_2
\end{align*}
\]

• \(\text{SiC/} \text{SiO}_2\) reaction

\[
\text{SiC} + 2 \text{SiO}_2 \rightarrow 3 \text{SiO} + \text{CO}
\]

• \(\text{Si}_3\text{N}_4/\text{SiO}_2\) reaction

\[
\text{Si}_3\text{N}_4 + 3 \text{SiO}_2 \rightarrow 6 \text{SiO} + 2 \text{N}_2
\]

3.1.7 *Metal carbides.* — Metal (zirconium, hafnium, titanium, tantalum, tungsten) carbides have very high TEC [35] and their oxides have high oxygen permeability. Therefore they are generally used in the temperature-pressure domain where the silicon carbide coating is not valid [36, 37] (chap. 3.1.6).

Chromium carbide deposits have been claimed to increase the oxidation resistance [38] but the stoichiometry of this carbide was not specified.

3.1.8 *Composite coatings.* — In order to adjust the coatings properties to the substrates, composite coatings have been developed. For instance, yttria-stabilized zirconia containing SiC whiskers [33], zirconium carbide and boron nitride [53], hafnium and silicon [54] have been deposited on carbon or carbon-carbon composites.

3.1.9 *Conclusion.* — The most common failure mechanism of a coating is its spallation due to the thermal expansion mismatch with the C/C substrate. To minimize the cracks, transition layers have been developed. Another way to protect the composite, and to limit the effects of cracks, is the use of glass formers (inhibited matrix) which are able to form mobile glass which spreads within the cracks.

3.2 *Transition layers.* — Carbide conversion layers improve surface cohesive strength. They are used beneath the outer coatings in particular for long or middle-term applications [36, 55-59, 63-65] (chap. 5). Most of the transition layers are made by a pack cementation process [60-61], and sometimes these layers are (boron or zirconium) doped [62]. This double protection (transition layer and outer coating) is efficient up to 1000 °C and 1600 °C for middle and short-term applications in a dry atmosphere.

Other intermediate layers such as porous CVD silicon layer [66] or graded coatings [53] have been developed but seem less effective.

Physical methods such as (boron) ion implantation have also been tested [53] in order to reduce oxidation rate at low temperature.

3.3 *Inhibited matrix.* — The oxidation protection concept with the use of a layer barrier is not valid when the damage probabilities are great (meteorite impact ...). Therefore a new approach has been developed by adding in the carbon precursor some glass formers which are able to spread within the cracks [38, 65, 67-71]. The most components studied are B₄C, B, CrB₂, ZrB₂, SiB₄, AlB₁₂, ZrH-Si, ZrB₂-Si, SiC, phosphates. With only inhibited matrix, C/C composites can be used up to 800 °C and to 1000 °C for middle and short-term applications.
respectively. This type of protection is generally used in addition to other protection systems [36, 55, 59, 63-65].


In order to protect the carbonaceous fibrous reinforcement, several coatings have been developed. Most of them have been applied by chemical vapor deposition [76-77] and by sol-gel methods [78].

5. Complex systems and multi-layer coatings.

In many aerospace applications, the desired properties of C/C composites are thermal stability, thermal shock resistance, oxidation resistance under thermal cycling conditions in a 1 atmosphere air pressure or in a partial pressure of molecular or atomic oxygen, resistance to degradation by moisture, resistance to rain erosion, high emittance and multi mission reliability.

In order to reach this objective, many complex systems have been developed including: coatings on fibers, inhibited matrix, transition layer, coating and outer glass sealant [73] (Fig. 5). Most of these oxidation protection systems contain SiC CVD coating on fibers, boron or silicon carbide in matrix, silicon carbide converted layer, silicon carbide CVD coating and outer silica (or borosilica) glass [51, 63-66, 73]. Another complex system has been studied by Bavarian et al. (Fig. 6). The protection is composed of a pyrolithic CVD carbon layer, a mixed hafnium carbide and hafnium disilicide layer and an outer silicon carbide layer. Unfortunately, these systems based on silicon carbide are not effective beyond 1800 °C in a dry atmosphere due to the active oxidation of silicon carbide (chap. 3.1.7). Moreover, in a humid atmosphere, this type of protection (which includes boron protection, as glass formers in the matrix or component of the outer glass) can only work up to 1100 °C for middle-term applications. Indeed, moisture absorption and subsequent rapid gas formation during heating led to the spallation of the coating from the substrate [73].
Other oxidation protections have been developed for high temperature and low gas pressure applications. Aerospatiale claims a double layer protection AlN/Al$_2$O$_3$ [74, 75]. Kowbel developed a system with the following features: a first diamond-like coating boron ion implanted, a second graded CVD ZrC-C layer and an outer mixed coating ZrC/BN [53] (Fig. 7). Fischbach [22] studied another complex system with an inner layer of a carbide-forming metal (Al, Hf, Zr), an impermeable metal barrier layer (Ir, Ru), and an outer layer of stable metal oxide former (Al, Hf, Zr).
6. Conclusion.

At present, many advanced oxidation protection systems have been developed but there is no universal solution for the general problem of protecting carbon-carbon against oxidation. The use of poisoning agents allows carbon-carbon to be protected up to 600 °C and 750 °C for middle-term applications and short-term applications respectively. At higher temperatures, external barrier layer must be used. However, due to the TEC mismatch between the coating and the substrate, oxidation protection must also include glass formers in the matrix, coatings on fibers, transition layers, oxygen barrier layer (carbide and nitride), outer glass sealant. With siliceous coatings, oxidation protection works up to 1800 °C in a dry atmosphere (1 bar) for middle-term applications. At higher temperatures or lower pressures, this system fails due to the active oxidation of silicon carbide. Boron compounds are good glass formers and used as outer glass sealants but they are too moisture sensitive which reduces the oxidation protection to middle-term applications up to 1100 °C. Thereby, there is a need for oxidation protection systems which are not moisture sensitive and which can work above 1800 °C for long term applications. It is possible that graded coatings and mixed layers could be developed with this objective in mind.

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