# OXIDATION STUDY OF CARBON-CARBON COMPOSITES FOR ACCELERATED LIFETIME TESTING

*Ilan Golecki[1]*, L. Xue[1], D.M. Dewar[2], A.F. Anderson[2], C.K. Duncan[2], J. van Horik[2], K. Eubank[2], T. Walker[3]*
*[1-3]AlliedSignal, Inc., USA: [1]Research and Technology, Morristown, NJ 07962; [2]Aerospace Equipment Systems, Torrance, CA 90504; [3]Aircraft Landing Systems, South Bend, IN 46628.*
**Phone (973) 455-4938; Fax (973) 455-4339 or -3008; E-mail: Ilan. Golecki@alliedsignal.com*

## Introduction and Motivation

Carbon-Carbon (C-C) fiber-matrix composite materials (C-C's) possess unique characteristics which make them attractive for a wide spectrum of current and potential applications: brake pads for airplanes and race cars, heat exchangers [1-2], re-entry missile cones, heat sinks for electronics and bipolar plates for fuel cells. C-C's have lower densities than aluminum (1.6-2.2 vs. 2.7 g/cm$^3$), and four times lower than stainless steel. C-C's have higher thermal conductivities than copper and the highest thermal conductivity per unit density among thermal management materials [1]. We have been developing aircraft C-C heat exchangers since 1995 under AlliedSignal internal funding. As described in a companion paper in this conference and in [1], we have demonstrated in-plane and through-plane thermal conductivities of 400-700 and 20-70 W/m.K in 0.2-0.8 mm thick, graphitized 2-D C-C panels. Panels with densities > 2.1 g/cm$^3$ and the desired rough-laminar carbon microstructure have been fabricated by chemical vapor infiltration (CVI) in one day. Tensile strengths up to 400 MPa have been measured. Cross-flow, 24x14x10 cm, high-density plate-fin heat-exchanger manifolded core modules have been fabricated and ground tested.

While C-C's can be used in a wide range of temperatures and in severe and chemically aggressive environments; they require protection from oxidation for continuous use above ~350°C in an oxidizing environment. The practical effect of oxidation is to diminish the structural and functional integrity of the article. As seen in Fig.1, aircraft heat exchangers may experience temperatures up to 700°C over a lifetime of ~ 10,000+ h. Thus, accelerated testing methods need to be developed, requiring, in turn, a detailed understanding of the oxidation mechanisms of both bare and protected C-C materials and structures.

More ordered and graphitic carbons oxidize at slower rates, all other considerations apart. In a C-C composite made of graphitic, pitch-derived fibers and of matrices derived from resin and from CVI, the fibers may be more oxidatively stable than the CVI matrix and the resin-derived matrix may be the least stable. The oxidation rate is also proportional to the exposed surface area and it increases with time in a linear-parabolic fashion, due to changing surface area. The thermal behavior in the surface-reaction controlled regime is exponential with temperature, with an activation energy of ~ 2 eV/molecule.

## Approaches to Oxidation Protection of C-C

Most published studies of oxidation protection of C-C's addressed the short time (~ 1 h)/high temperature (> 1200°C) domain for > 5 mm thick articles. We are studying the long time/intermediate temperature regime (Fig. 1) for much thinner articles. In this regime below 700°C, there are many barrier coating materials, e.g., SiC, $Si_3N_4$ which do not oxidize and <u>if intact</u>, would prevent oxidant incursion into the underlying C-C.

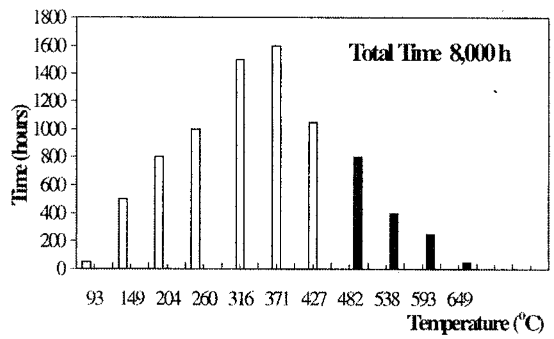


**Figure 1.** Typical time-temperature profile for an aircraft heat exchanger.

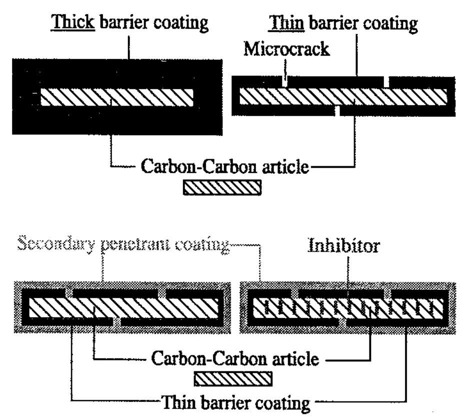


**Figure 2.** Types of oxidation protectors for Carbon-Carbon under evaluation at AlliedSignal.

However, due to the very low coefficient of thermal expansion (CTE) of C-C's, -1 to +1 ppm/°C in the fiber plane [see companion paper and Ref.1] and the resulting CTE mismatch with most coating materials (e.g., CTE of SiC = 2.8-5 ppm/°C ), <u>microcracks</u> may develop in the barrier either during cooldown from deposition or during subsequent service. Issues directly bearing on the formation and density of microcracks include the barrier thickness, deposition method and thermal budget.

In order to augment the effectiveness of the "barrier" material, a secondary glass overseal or penetrant is used. This glass softens in the use temperature regime and provides the required sealing of the voids in the barrier as well as those in the C-C article. As shown in Fig. 2, in some cases it may be necessary to include a third component in the oxidation protection scheme in the form of a matrix inhibitor.

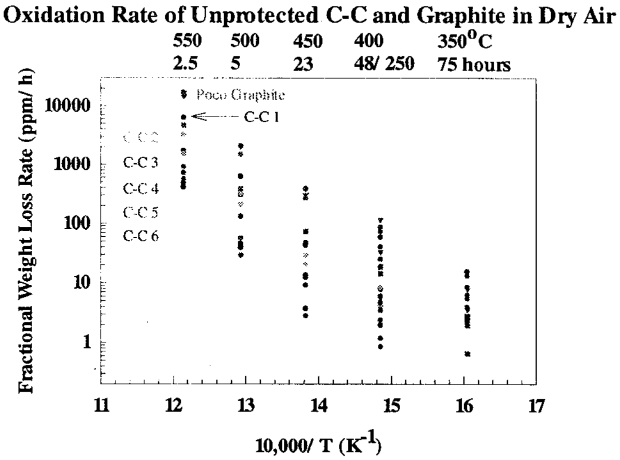


**Figure 3.** Fractional weight loss of several sets of bare, fully processed, pitch-derived C-C coupons in flowing dry air.

Application methods of oxidation protectors into and onto C-C articles under evaluation at AlliedSignal include:

* CVD, which provides good penetration and uniform surface coverage of complex parts. One drawback is the relatively high application temperature of ~ 600-1000°C, leading to potential microcracks upon cooling due to thermal mismatches.

* Plasma-enhanced CVD, which enables a lower deposition temperature (<400°C) than CVD and thereby reduces the effect of CTE mismatches: $\varepsilon_f = (\alpha_f - \alpha_s)(T_{dep} - T_o)$.

* Liquid precursors, which enable incorporation of particulates but require thermal annealing at moderate/high temperatures.

## Results

As a part of a baseline study, we have measured the oxidation rate in flowing dry air of relatively large size, bare, fully processed and heat-treated, single-, two- and three-ply, 2-D pitch-fiber C-C and Poco graphite coupons. The results (Fig. 3) show that different materials and fabrics oxidize at very different rates. Some sets have very low oxidation rates even without any protection. Poco graphite exhibits higher oxidation rates than our C-C's. Different C-C's also exhibit measurable differences in the activation energies, even though all have been annealed at nominally the same high temperature. Additional data are required at the lowest temperatures to improve the measurement sensitivity. At the highest temperatures, there may be non-linear behavior with oxidation time due to the changing surface area. These results are interesting scientifically and have enormous practical significance.

For oxidation-protected C-C's, our goals are to demonstrate survivability of articles under realistic time-temperature profiles; study and develop an understanding of the oxidation mechanisms of variously protected C-C materials to enable accelerated lifetime testing; implement novel testing methodologies and correlate these with weight changes and mechanical properties. Weight change data vs. time and temperature for two coatings and several types of C-C coupons are shown in Fig. 4 and 5. These coated C-C coupon sets show no weight loss after 300 h at 650°C, as well as after exposures of hundreds of hours in a range of temperatures from 450 to 650°C. While the lack of weight loss does not preclude some carbon oxidation during the air exposure,

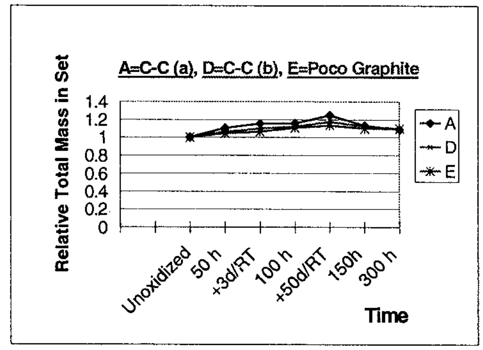


**Figure 4.** Weight changes of two sets of coated, fully processed and heat treated, pitch-derived C-C coupons and one set of coated graphite coupons in flowing dry air at 650°C.

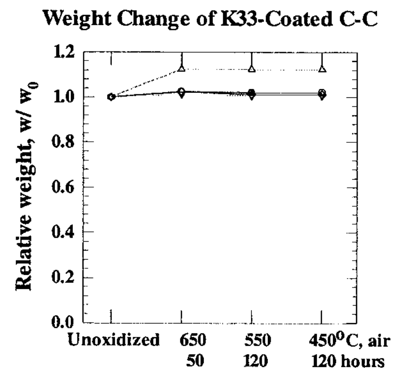


**Figure 5.** Weight change of four sets of coated, fully processed and heat treated, pitch-derived C-C coupons in flowing dry air.

it is nonetheless a very promising result. Mechanical tensile strength testing will be performed.

## Summary

We have demonstrated survivability with no weight loss of coated C-C heat-exchanger articles in flowing air at 450-650°C over hundreds of hours. Methodologies have been developed for applying different types of coating systems to complex-shaped C-C articles. Several approaches to the non-destructive characterization of the effects of C-C oxidation are being implemented. Our approaches for protecting C-C parts from oxidation exhibit excellent potential as producible solutions for C-C heat exchangers to 650°C and above.

## References


1. I. Golecki, L. Xue, R. Leung, T. Walker, A. Anderson, D. Dewar, C. Duncan and J. van Horik, "Properties of High Thermal Conductivity Carbon-Carbon Composites for Thermal Management Applications", in Proc. 1998 High Temperature Electronic Materials, Devices and Sensors Conference, San Diego, CA, Feb. 1998, IEEE, Piscataway, NJ, 1998, pp.190-195, I. Golecki, E. Kolawa and B. Gollomp, Eds.
2. A.F. Anderson, D.M. Dewar, C.K. Duncan, M. Fellman, I. Golecki, W.F. Maudru, T.B. Walker and L. Xue, "Carbon/Carbon Heat Exchanger and Manufacturing Method", European Patent EP891530A1/WO97/30321 (1999). Dewar, A.F. Anderson and C.K. Duncan, U.S. Patents 5,626,188; 5,628,363; 5,655,600 (1997); 5,845,399 (1998).