STRENGTH ENHANCEMENT AND APPLICATION DEVELOPMENT OF CARBON FOAM FOR THERMAL PROTECTION SYSTEMS

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ABSTRACT

Carbon foam is recognized as having great potential as a component within hybrid (rainbow) Thermal Protection Systems for low angle re-entry vehicles. In this concept, the carbon foam supports a ceramic matrix composite surface by providing selectable insulating or thermally conductive dual-use properties. An initial barrier to implementation was the inherent weakness and friability of the carbon foams. Under a MDA funded SBIR program, Ceramic Composites Inc. has demonstrated the ability to increase the compressive modulus by 2½ times through the treatment of the carbon foam ligaments with a uniform silicon carbide coating, serving to enhance strength and reduce friability, with minimal influence upon the thermal properties. The process is scaleable to leading edge sizes using commercially available equipment. An overview of the technical approach will be presented, along with the envelope of enhanced material properties achieved under the program.

INTRODUCTION

Carbon foams of various pedigrees have been studied since the late 1960s when the first reticulated foams were produced.[i] These foams were thermally insulating and remained so for many years. In the 1970s, research focused primarily upon producing carbon foams from alternative precursors. In the early 1990's, researchers at the Wright Patterson Air Force Base Materials Lab pioneered mesophase pitch derived graphitic foams, specifically for replacing expensive 3-D woven fiber performs in polymer composites and as replacements for honeycomb materials. This was one of the first high thermal conductivity carbon foams and the technology was licensed by MER Corporation of Tucson, AZ. Later, West Virginia University developed a method that used coal as a precursor for high strength foams with excellent thermal insulation properties, a process licensed by Touchstone Research Laboratories of Triadelphia, WV. Ultramet produces a similar product of thermally insulating pyrolitic CVD carbon on reticulated vitreous carbon cells.[ii] In 1997, James Klett at the Oak Ridge National Laboratory (ORNL) reported the first graphitic foams with bulk thermal conductivities greater than 40 W/m·K (Figure 1). This process was licensed to POCO Thermal Materials of Decatur, TX and the product trade named POCO Foam. POCO later developed POCO HTC, which has higher thermal conductivity and density. The POCO materials are made in sheets, similar to cakes, with properties in the Z-direction radically different than in the x-y directions.

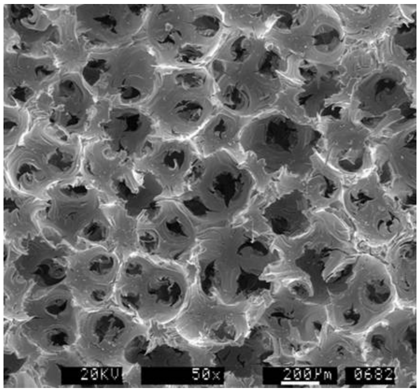

Figure 1: Micrograph of ORNL carbon foam.

These recent carbon foams are of interest due to their high thermal conductivity (primarily in the z-direction), low density, and open cell structure. With thermal conductivities similar to aluminum, they are under consideration for thermal protection systems, thermal management systems (both active and passive), solar radiators, industrial heat exchangers, electronics cooling, and noise absorption. In Thermal Protection Systems (TPS) there are two approaches under consideration for utilizing carbon foams. Allcomp Inc.[iii], Materials and Electrochemical Research[iv], Touchstone[v], Ultramet[vi], Fiber Materials Incorporated[vii] have suggested placing *insulating* carbon foam below a Ceramic Matrix Composite (CMC) shell to protect the craft interior from the heat of re-entry. This is shown in the left view of Figure 2. Thompson[viii] of San Diego State University suggested the use of *high thermal conductivity* carbon foam to distribute the thermal load from the leading edge to the cooler, aft portions of the structure and/or transfer the heat to active cooling features imbedded within the carbon foam (Figure 2). This concept may also take advantage of the preferential thermal conductivity in the z-direction to move the heat aft while partially insulting the interior.

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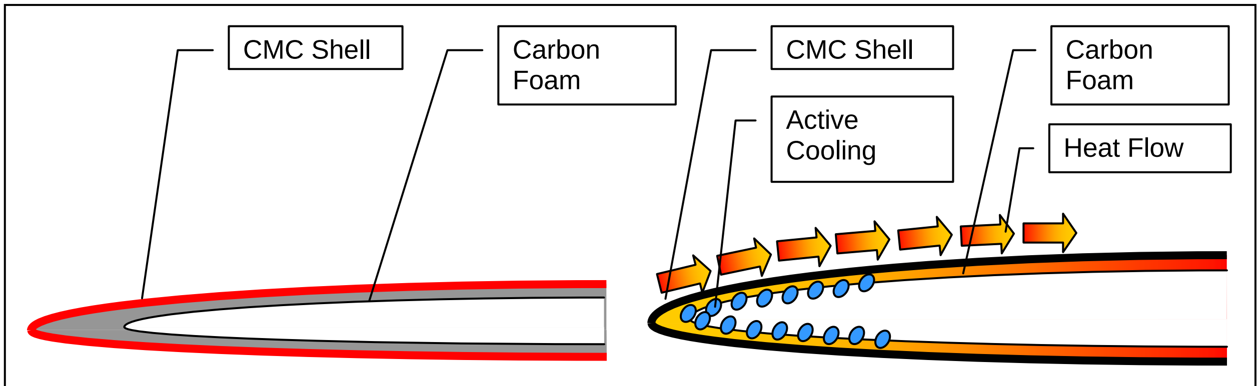

Figure 2: Insulating (left) and conducting (right) applications of carbon foam to thermal protection systems.

The implementation of carbon foam into these various thermal management systems has been prohibited by its inherent low strength. The material properties reported by the various manufactures of carbon foams are listed in Table 1 and the low compressive strengths clearly stand out. This makes the carbon foam difficult to work with, friable, and subject to physical damage during use. Previous attempts to enhance the strength of carbon foams have focused upon altering the processing parameters or precursors, or upon coating the foam ligaments with a supportive material. Ultramet[ix], et al have experimented with coatings of CVD SiC, CVD mullite, CVD Si-B-C, polymers and metals. Each of these approaches has produced composites which have negatively affected the thermal conductivity of the product, added excessively to the mass, or reduced the thermal operational limit. The CVD approach also has a tendency to preferentially deposit on the exterior surfaces of the foam block, leaving a gradient coating, placing a limit upon the cross-section of preforms. Slowing the deposition rate to achieve a more uniform coating, exponentially adds time and cost to the process.

Table 1: Reported carbon foam properties.

PROPERTY	POCO Foam	POCO HTC	MER	Touchstone CFoam
Density (gm/cc)	0.56	0.90	0.19 – 0.80	0.27 – 0.40
Thermal Conductivity (W/mK)				
z-direction	135	245	0.05 - 210	0.25 – 70
x-y direction	78	70		
Compressive Strength (MPa)	2.1	5.9	0.25 - 7.0	4.8 - >15
Total Porosity (%)	70	61	64 - 99	82 – 88
Open Porosity (%)	96	95		
Avg. Pore Diameter (µm)	350	350	30 – 1270	

STRENGTH ENHANCEMENT

Enhancement Approach

Ceramic Composites Inc. (CCI) elected to take an alternative approach to enhancing the strength of carbon foam. For our evaluation, two polymeric pre-ceramic precursors which convert to silicon carbide when fired were selected, Previously used to enhance the fabrication of structural composites materials, these precursors can be fired to a low or high temperature, yielding an amorphous or crystalline beta silicon carbide, respectively. The first polymer is Starfire®[1], an allylhydridopolycarbosilane (AHPCS), designated as Polymer A. A version of this polymer modified with the addition of 2% butoxide was also evaluated and designated A+. VL20[2], a polysilazane designated herein as polymer B. The typical methods of part infiltration is dilution of the precursor with solvent or vacuum infiltration of the preform within a mold, curing at low temperature to release the organic volatiles, followed by

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[1] Starfire Systems, Malta, NY
[2] Kion Corporation, New York, NY

repeated infiltrations before firing at an elevated temperature. As the goal was not the formation of a solid matrix, but rather an enhancement coating, this process was altered to allow the excess infiltrant to drain from the preform prior to curing. Thus, based upon the test parameters listed in Table 2, CCI undertook the study of a wide variety of samples.

Test Results

Micrographs. Microscopic evaluation of the samples revealed a thin coating of silicon carbide one the surface of the carbon ligaments with accumulations of silicon carbide at the ligament fillets as seen in Figure 3.

Mechanical Testing: The densities of the samples follow the typical trend seen for composite materials where the amount of increase with each subsequent infiltration reduces (Figure 4). If we were attempting to produce a fully dense sample, the parts would be fired to an elevated temperature after the third infiltration before continuing. The difference in density has a dramatic influence upon the ability to flow coolant through the sample and this will be discussed later in this article. Compressive and four-point flexural testing of the samples were performed. Not surprising, the latter produced widely scattered data and is not presented. Figure 5 illustrates that the use of a lower concentration of polymer affected the compressive strength, with the 5, 7 and 100% concentrations demonstrating progressive increases. The use of the additive did not appear to affect strength

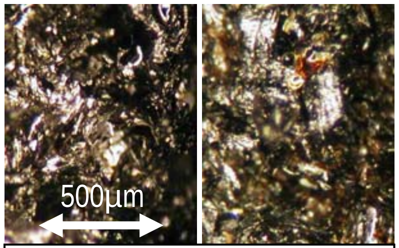

Figure 3: Micrograph of neat and infiltrated carbon foam.

Table 2: Test matrix variables.

PARAMETER	VARIABLE
Carbon Foam	POCO HTC
Infiltrates (pre-ceramic polymers)	Polymer A
	Polymer A plus additive
	Polymer B
Firing Temperature	Low (amorphous)
	High (crystalline)
Infiltration Cycles	Zero, One, Two, Three
Infiltrate Concentration	7%, 5% and 100% respectively

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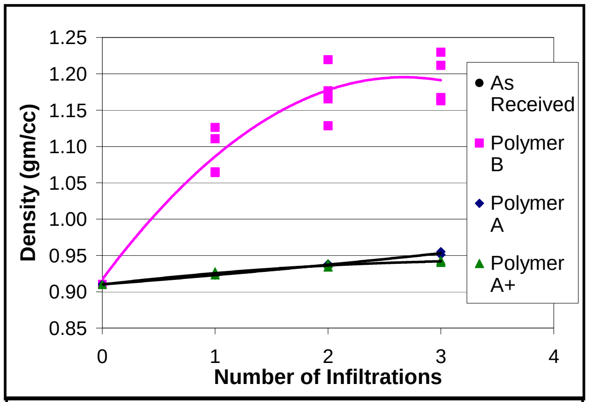

Figure 4: Densities of enhanced POCO HTC Carbon Foam.

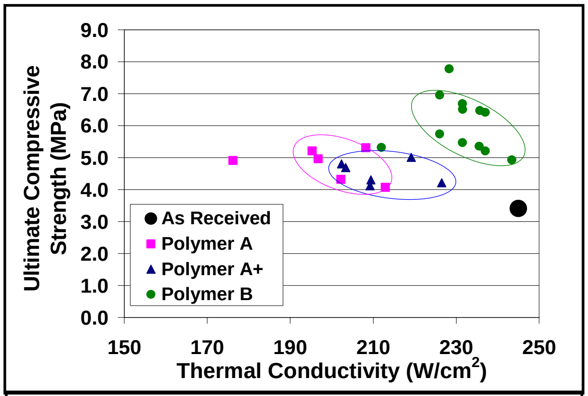

Figure 5: Sample strength and thermal conductivity results.

Hot Plate Testing: The thermal properties of the enhanced carbon foams were measured using the guarded hot plate method. The use of the additive in Polymer A appeared to enhance the bonding between the carbon foam and the ceramic coating, increasing the conductivity despite the lower polymer concentration. Even so, the use of the 100% concentration with Polymer B demonstrated superior performance. Furthermore, firing the B polymer to the higher temperature clearly increased the thermal conductivity of the samples. Little effect of firing temperature was noted for polymer A. However, this could be due to proportionally closer results and a lack of definition in the test method.

Flow Testing: Coolant flow *through* the carbon foam is of importance to aerospace design engineers as the thermal transfer capability is increased by a factor of ten, compared to flow *past* carbon foam fins.[x] Flow testing was performed on 25.4-mm diameter by 25.4-mm thick samples in the x-y direction with both water and nitrogen gas, using the apparatus shown in Figure 6. The data is shown in Figure 7 and reveals a strong relationship between the density of the sample and the ability to flow coolant. The samples infiltrated with Polymer B were unable to flow water, but exhibited an 85% correlation of gas flow rate with density. Select sample infiltrated with Polymer A and A+ exhibited similar or superior flow capabilities to neat foam with both water and gas. The ability to maintain flow through the sample allows the design engineer to perform a trade study between coolant pressurization and heat exchanger performance. It is suspected that the flow-by cooling will be similarly affected.

Figure 6: Water and gas flow test apparatus.

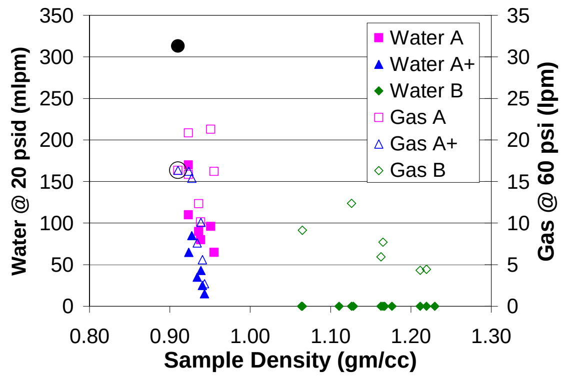

Figure 7: Flow testing data.

Thermal Impedance Testing: Anteon Corporation has previously performed testing of the thermal impedance of carbon foam and additional work was performed in this study.[xi] Using the apparatus shown in Figure 8, samples of enhanced strength carbon foam which pass coolant in the flow tests were selected for impedance testing. Unfortunately, the Anteon test facility was unable to force coolant water through the samples, so a bypass approach was undertaken. Nevertheless, the results attained were interesting. As water passes below the carbon foam, power is applied to the thick film resistor and the ability of the carbon foam to remove the heat energy was recorded using an infrared camera. This digital data was converted to a thermal impedance value using the formula:

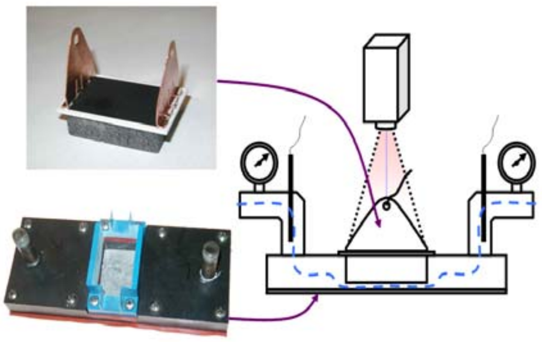

Figure 8: Anteon thermal impedance test fixture.

$$\theta_{(x,y)} = \frac{T_{(x,y)} - T_F}{(Q/A_{SAMPLE})} \tag{1}$$

where θ represents the thermal impedance, T the temperature of the sample at point (x,y) or the temperature of the fluid, and (Q/A), the heat flux. From the resulting data, maps of the heat dissipation of the sample were generated as shown in Figure 9 and thermal impedance plots were developed as a function of water flow rate and applied power as shown in Figure 10. The data for the samples infiltrated with polymer A exhibited a 10 to 33% increase in thermal impedance and, similar to CCI's results for thermal conductivity, the Polymer B samples are projected to exhibit only a 5% increase.

Figure 9: Graphics of thermal impedance testing at 600 W of neat foam at 3.5 and 2.0 gpm and a coated sample at 2.0 gpm.

SUMMARY

Through the application of a silicon carbide coating, via polymeric precursor, to the carbon foam, a uniform ligament coating has been applied to the structure which increases the compressive strength by up to 2.5x while reducing the thermal conductivity by only 5%. This level of performance enhancement is greater than that known to be achieved by any other means. A tailorable range of properties is achievable with this approach and the approach should be applicable to any commercially available open celled carbon foam. Additional work is suggested to refine the concentrations of polymer and determine their impact upon performance. Finally, with the strength and friability of the foam reduced, it is suggested that effort be shifted from enhancement to application demonstration.

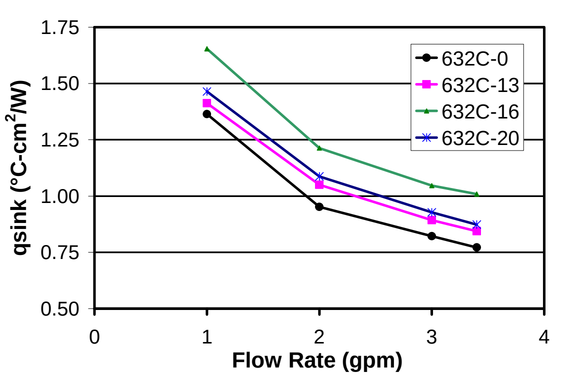

Figure 10: Thermal impedance data.

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