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for
CRADA Number ORNL-02-0664

Between

UT-Battelle, LLC

and

Synterials, Inc.
(Participant)

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For the Participant:

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Project Engineer
(Title)

June 25, 2007
(Date)

OAK RIDGE
NATIONAL LABORATORY
MANAGED BY UT-BATTELLE
FOR THE DEPARTMENT OF ENERGY

CRADA No. ORNL-02-0664

With Synterials, Inc. for
Intermediate Temperature Carbon – Carbon Composite Structures

Final Report

UT-BATTELLE

ORNL-27 (4-00)

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Intermediate Temperature Carbon – Carbon Composite Structures

Final Report

Abstract
The objective of this Cooperative Research and Development Agreement (CRADA) between UT-Battelle, LLC (the "Contractor") and Synterials, Inc. (the "Participant") was to demonstrate promising processing methods, which can lead to producing Carbon-Carbon Composites (CCC), with tensile and interlaminar properties comparable to those of organic matrix composites and environmental stability at 1200°F for long periods of time. The participant synthesized carbon-carbon composites with two different fiber coatings and three different matrices. Both parties evaluated the tensile and interlaminar properties of these materials and characterized the microstructure of the matrices and interfaces. It was found that fiber coatings of carbon and boron carbide provided the best environmental protection and resulted in composites with high tensile strength.

Purpose and Background
The purpose of this Cooperative Research and Development Agreement (CRADA) between UT-Battelle, LLC (the "Contractor") and Synterials, Incorporated (the "Participant") is to demonstrate promising processing methods, which can lead to producing Carbon-carbon Composites (CCC) with tensile and interlaminar properties comparable to organic matrix composites and which are stable at 1200°F for long periods of time.

Carbon-carbon composites (CCC) have been developed and used for high temperature structural applications. They have been successfully used for the leading edges of the space shuttle, rocket nozzles and for aerospace vehicle brakes. These applications take advantage of the lightweight, high refractoriness and moderate raw materials cost, inherent in these carbon-derived materials. However in all cases, CCC parts are life limited by their poor oxidation resistance.

As discussed in some detail in *"Carbon-Carbon Composites- A Historical Perspective"*, by Donald L. Schmidt, oxidation protection systems for CCC were developed in the 1970's and 1980's. They tended to include three approaches:

- Ceramics Coatings
- Matrix Inhibitors
- Sealants

Ceramic coatings were typically silicon carbide or silicon nitride, prepared by chemical vapor deposition (CVD). Because of differential thermal expansion between the CCC and the coating, most coatings would contain cracks that permitted

access of oxygen to the matrix. Silicon nitride has a lower coefficient of thermal expansion than silicon carbide, so the extent of crack opening in silicon nitride is less than that for silicon carbide.

Matrix inhibitors have included fine powders of various carbides when the matrix is made by resin derived methods and also when chemical vapor infiltration (CVI) methods are used. The inhibitors are often boron carbide, silicon carbide or zirconium boride. Inhibitors become active when the coating or sealants fail and the matrix is exposed to oxidizing conditions. The inhibitors oxidize to form glassy oxide surfaces, which tend to heal cracks in the sealant layer or the CVD coating. In addition to matrix inhibitors, the surface of the densified carbon matrix is often converted to silicon carbide via vapor diffusion controlled conversion process.

The sealant layers are applied as thin films made from liquid precursors, often using sol-gel technology. Tetraethylorthosilicate (TEOS) and other organometallic precursors have been used to produce silica or borosilicate glass sealants. Once the glass is formed and melts it also can soften and seal cracks providing a protection against oxidation.

For applications where temperatures reach above 1600°F, these systems can be made to work reasonably effectively. However, the oxidation protection systems are least effective in the temperature range of 700°F to 1200°F. In this temperature range, temperature is not high enough to activate the formation of liquid phases i.e., to melt glasses or oxidize the carbide phases to form boron oxide glasses. Therefore conventional approaches to processing CCC will not result in oxidation resistant, high strength CCC.

Therefore, the objective of this project is to demonstrate promising processing methods, which can lead to producing Carbon-Carbon Composites (CCC), with tensile and interlaminar properties comparable to those of organic matrix composites and environmental stability at 1200°F for long periods of time.

Results

To screen the properties of composites with different fibers, mini-composites (single tow composites) were prepared using the Borden SC1008 phenolic resin. In addition, a blend of 50-weight% SC1008 phenolic resin and 50-weight% Starfire polysilane resin was also used to prepare mini-composites. The tows were kept straight by clipping a small weight on the lower ends of the tow during B-staging at 160°F and then curing at 350°F. It was observed that after additional curing to 500°F for 16 hours, the minicomposites did not warp during subsequent treatments at higher temperatures.

Four fiber types were used to prepare composites from the two matrices. The fibers included:

- Uncoated T-300
- C-B_4C coated T-300

- Uncoated P-55S
- Uncoated IM7

The single tow composites were then heated to 1550°F (860°C) in argon for 1.25 hours in order to pyrolyze the resin matrices. The 1550°F temperature was established to promote a stable char in the two resins but to minimize the extent of matrix shrinkage.

Task 2.0 Coating of Composites

Some minicomposites were subsequently coated with Si_3N_4. The coating was deposited by using flowing $SiCl_4$ and NH_3 gases at 800°C and a pressure of 1.0 torr. Coatings of Si_3N_4 for oxidation protection of C-C composites are often as thick as 250 micrometers. However the thickness of these coating was less than 200 nm and the coating was expected to be amorphous rather than crystalline.

Task 3.0 Mechanical Properties and Microstructure

Tensile testing of the cured tow was completed for the SC1008 resin composites. Cured mini-composites were bonded to a manila picture frame and then clamped in the metal fixture and loaded in tension until fracture. The picture frame is cut prior to testing. Strength was calculated based on the cross sectional area of the fiber tow. No strength was attributed to the strength of the matrix. Table 1 lists the average of the breaking load for 3-6 repetitions for each condition.

Pyrolyzed minicomposites and pyrolyzed plus Si_3N_4 coated minicomposites were tested in a small fixture developed at Oak Ridge National Laboratory. The ORNL test fixture used a 1-inch gage length and gripped the tows with epoxy in a pop-rivet. The advantage of this method is uniform single point loading of easily manipulated specimens with little tendency for flexing during sample loading. Table 2. summarizes the results of testing for five specimen types. These results indicate that the coating on the interface coating on the T-300 fiber promotes a high percentage of retained strength than without the coating.

Table 1. Tensile Strength of Cured Mini-composites

Fiber Type	Ave. Load,(lb.)	Ave. Strength, (ksi)	Fiber Dia.,(micron)	Fil./Tow
Uncoated T-300	64.3	369	7	3k
Coated T-300*	42.7	245	7	3k
P-55S	118.6	212	10	4k
IM7	75.7	536	4.5	6k

* T-300 coated with a C-rich boron carbide

Table 2. Summary of Tensile Strength of Single Fiber Composites

Fiber Type	Matrix	Pyrolyzed Comp.	% Retention	Coated+Pyro.Comp.	% Retention
T-300	Phenolic	241 ksi	65	142 ksi	38
Coated T-300	50-50	273	73	209	57
P-55S	Phenolic	95	45	74	35
P-55S	50-50	88	42	82	39
IM7	50-50	332	62	248	46

Table 2. lists the tensile strength of composites after the pyrolysis process step and also of composites, which were pyrolyzed and coated with Si_3N_4. The percent retention is with reference to original strength of the each category of fiber prepared with a cured phenolic resin matrix. In the case of the coated T-300 fiber the strength of the coated fiber was only 66% of the strength of the uncoated fiber shown in Table 1. The indicated strength of the pyrolyzed composite was actually higher than the as coated T-300. More significantly, the strength retention of the pyrolyzed and Si_3N_4 coated specimens had the highest percent of strength retention of all of the materials. The second highest strength retention was for the IM7 material. Specimens of those materials had a higher total strength even without the coating at 248 ksi. More work should be done to investigate a carbon rich boron carbide coating on that fiber.

Tests were also conducted to determine the effect of oxidation on the properties of the composites. Oxidation tests were carried-out in an air furnace with tows of the coated fibers. These oxidation results coupled with the retained strength results certainly indicate the relative value of the C-B_4C interface coating. Oxidation testing was not performed on the composites as time and funding did not permit completion of that part of the program. Synterials does intend to pursue the C-B_4C interface coating on graphite fibers for carbon-carbon composites and for carbon reinforced CMCs.

Subject Inventions

None Produced under this CRADA

Conclusions

- 2-D composites fabricated with un-coated T-300 fabric and Borden SC1008 phenolic resin produced well-consolidated composites. However, panel fabricated with boron nitride/silicon nitride interface coated fabric produced exfoliated composites after curing under pressure.

- A desire to investigate other fibers which might produce higher strength carbon-carbon composites and the need avoid exfoliation problem in composite fabrication lead to a decision to prepare and test single tow composites.
- Two additional graphite fibers, P-55S and IM7, were introduced into the program. The selection of these fibers was based upon their relatively low thermal expansion in the radial direction. This would minimize de-bonding of the interface coatings from fibers and matrices.
- Two matrix compositions were investigated: the standard phenolic and a blend of 505 phenolic and 50% polycarbosilane from Starfire. No significant difference in results of strength tests was observed.
- A group of specimens also evaluated a thin over coating of CVD Si_3N_4. In all cases, the presence of the coating did degrade the strength of the single tow composites compared to no coating on the composite. However the effect of the coating on oxidation behavior was not evaluated.
- The highest strength composites that received the full processing of pyrolysis plus Si_3N_4 coating, was the IM7 fiber with the 50-50-matrix composition.
- The highest percentage retention of tensile strength was the T-300 fiber with a carbon rich boron carbide coating.

Recommendations for future work

Investigating the use of C-B_4C coatings on IM7 fibers, the validation of the conclusions listed above with multi-layer 2D composites and a full investigation of mechanical properties at elevated temperature.