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To: Distribution

From: Douglas S. Mehoke

Subject: ACF Material Development Study Summary Report

Reference: NASA/TM-2020, Final Contractor Report, “Development of Light-Weight, High-Temperature Materials”, John E. Garnier, Matthew E. Currie, Shawn L. Perkins, September 2020.

This memo summarizes the Advanced Ceramics Fibers, LLC final report on their study on the development of light-weight, high-temperature materials under the Interstellar Probe (ISP) project. The referenced report distribution rights are limited. This summary presents an open rights version of the study. The material, processing, and testing information detailed in the referenced ACF report is only summarized here. The ACF report provides the full details of their work.

Summary

The principal enabling design element for a near-Sun Oberth maneuver is the development of a light-weight, ultra-high-temperature (UHT) material for the solar shield. A 7 month, Phase I, materials research and development effort into potential options for this type of material was conducted by Advanced Ceramic Fibers , LLC (ACF). The goal of the study was to develop a material that could survive a near-Sun pass of less than 3 solar radii (Rs). The pass would require the material to survive temperatures of above 3000°C for more than a few hours. The results of the study showed the potential for materials to survive up to 3500°C.

The optical properties of the surface drive its temperatures and are difficult to control, or measure, at high temperatures. For the study, it was assumed that a solar absorptivity/IR emissivity, α_S/ϵ_{IR}, in the range of 0.6 to 1.1 would be possible. The candidate materials selected by ACF have their optical properties in this range, and those properties may be tailorable. Shield temperature profiles, along with the testing limitations at high temperature are shown in Figure 1.

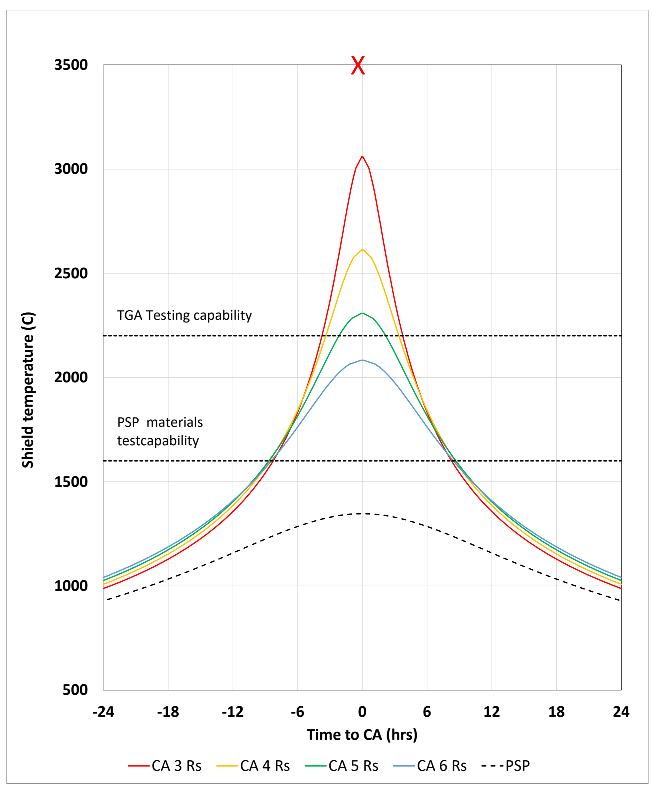

Figure 1. Near-Sun pass shield temperature profiles and testing capabilities

Because the ISP shield will be very large (10's of m^2), a light-weight, structural material is critical to keep the mass of the shield viable. A nominal shield design would consist of a UHT outer shield layers, a PSP-like C-C/foam section, and the supporting structure. Mass goals for the shield were set at between 30 kg/m^2 to 60 kg/m^2. The use of known UHT material, such as tungsten, would make the shield too heavy to be feasible. The candidate materials developed by ACF are light-weight enough, 2 g/cm^3 to 5 g/cm^3 density range, and may retain enough mechanical strength to make a near-Sun shield possible.

The ACF study builds off their work done under their Office of Naval Research (ONR) Small Business Innovation Research (SBIR) Phase II SiC ceramic matrix composites (CMC) Project. The focus of the new study was to see if the ACF processing techniques could be extended to include the use of UHT refractory carbides. These carbides share several very unique properties; they contain some of the highest melting substances presently known, and most of the compounds are hard and chemically inert. Potential materials for the study included BN, NbC, ZrC, TaC, and Re_2C.

Technical Results

Several interesting generalities occur in carbides of the nine transition-metal elements (Ti, V, Cr, Zr, Nb, Mo, Hf, TA, and W). The highest carbide phase, which is in equilibrium with graphite, is either fcc or will convert to this form before melting. The composition range of the "hexagonal" structure is relatively narrow, although the cubic form can exist over an amazingly wide range. This phenomenon is caused by vacant positions in the carbon lattice and not by interstitial solution of the metal or a lower carbide. The highest melting point within the group occurs for TaC, with a value in excess of 4000°C. All of the carbides begin to rapidly evaporate both metal and carbon atoms near their melting temperature.

Testing of temperatures for UHT material testing exceedingly difficult. Multiple temperature testing options were considered including two-color pyrometry, disappearing filament pyrometry, and filament mass loss. Two-color pyrometry is a common method used to measure high temperatures. Commercial units are available with data sheet ranges over 3000°C. Disappearing filament pyrometry measures temperatures by comparing a glowing samples to the light of a heated filament. It was has been used since the early 1900s to measure temperatures above 1000°C and has been used up to 3000°C. Finally, in heated-filament, mass loss measurements, a filament is heated to a constant temperature for a specific period of time. The reduction in diameter of the filament, coupled with the known vapor pressure of the material is used to determine the temperature of the sample.

For this study the main temperature measurements were made using the disappearing filament technique. It is important to note that the development of a calibrated, UHT measurement capability was beyond the scope of the study, so the techniques used remain in need of additional refinement to demonstrate accuracy and repeatability. However, the temperatures measurements taken, along with predicted mass loss for those materials at the given temperatures, indicate samples successfully survived above 3500°C.

The ACF samples were tested both using torch testing and vacuum heating. The proprietary process developed by ACF produces a metal carbide with a very low vapor pressure and low density. As the ACF study was an early one, aimed to show the potential for their new process to fabricate materials capable of surviving to 3000°C, the original plan was to subject the new samples to heating using an oxygen-acetylene torch. Depending on the proportions of oxygen and acetylene used, the torch produces flame temperatures up to about 3500°C. Samples survived this test, but knowledge of the actual temperatures achieved was limited. Also, the testing was done in an ambient atmosphere that had the potential to induce its own material changes.   Therefore early on in the study ACF began the development of a more controlled test capability.

A vacuum, resistive heating teat system was built capable of "more realistic" UHT testing.   Using the test system shown in Figure 2, developed as part of the study, test samples could be electrically heated to around 4000 C in vacuum.

- Power input was up to 1500 watts AC, heating.
- Vacuum: up to 10(-6) torr.
- Temperature: Disappearing (W) Filament Pyrometer. HT lens series (T to 4000 K). Tungsten Calibrated.

The ACF Resistive Heating System continued to be upgraded throughout the study and was used for all UHT testing. At Project start, the need to test for optical properties was recognized, but not performed due to the unavailability of JHU/APL testing facilities. Materials emissivity is very important to the determination of actual temperature. ACF used public literature data to determine a range of metal carbide emissivities and a Disappearing Filament Pyrometer using a tungsten standard. Based on sample "brightness" compared to the tungsten, a "small" sample temperature could be directly measured with the need for a background correction followed by an emissivity correction to a "true" temperature within a +/- error range.

Other material testing performed included post-test SEM, EDS inspection of the coupons to validate the material containment mechanism for suppression of vaporization. Also, mechanical tests on fabricated sample coupons were performed to indicate strength and modulus. Material coupons showed good 'toughness", and 4-pt Bend Test strengths to 20 Ksi. These test were done on single or small sample sizes, and while not usable to develop mechanical performance, clearly indicate the effort achieved the project goal of developing materials with low vapor pressure, low density, and reasonable mechanical strength.

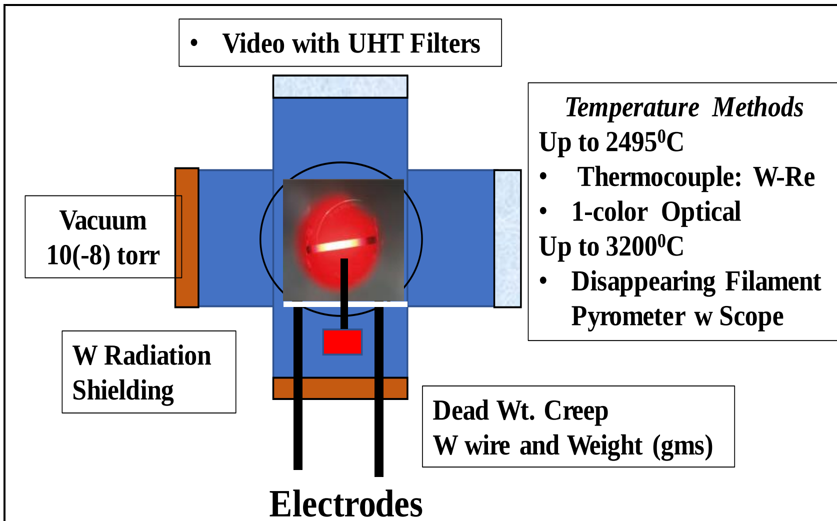

Figure 2.   ACF Resistive Heating System for heating small samples to UHT in vacuum or controlled atmosphere.

The key focus of the study was to develop materials with low vapor pressures at high temperatures. Based on the PSP experience, a good material for the design of high temperature shields is C-C. Based on literature data, vapor pressures for carbon and some metal carbides are shown in Figure 3.

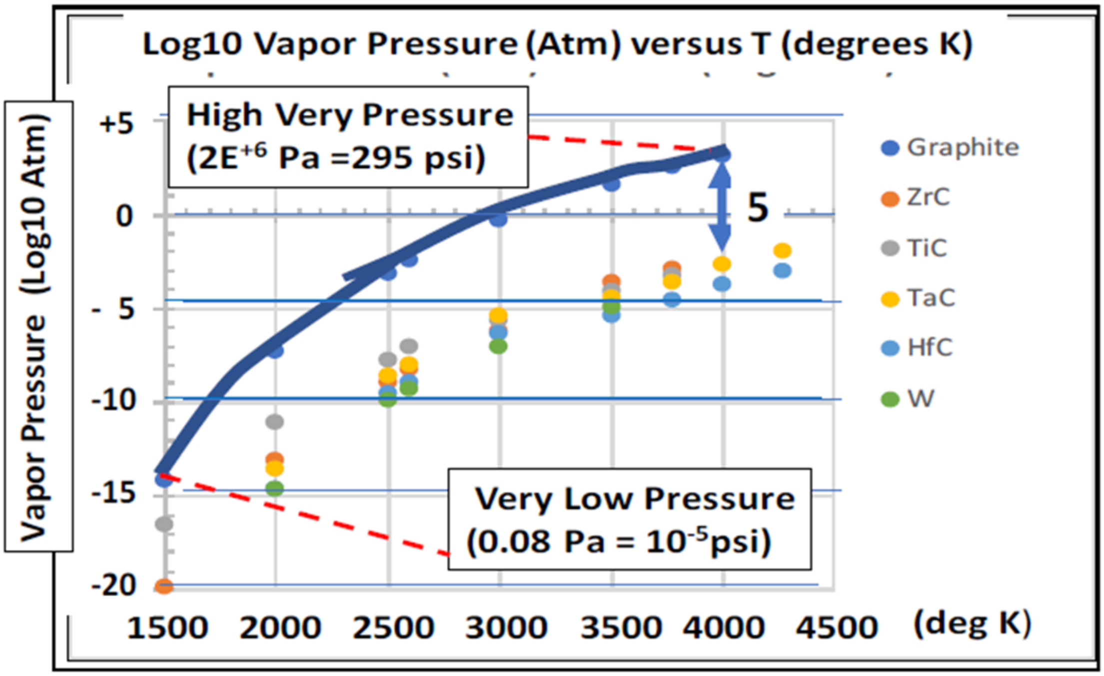

Figure 3. Vapor Pressure versus temperature for carbon and metal carbides

For a near-Sun ISP approach, the meaningful upper limit for a carbon thermal shield is about 2300°C. Around that temperature, material mass loss will cause the shield to disappear during the pass. Metal carbide vapor pressures, taken from literature, are also shown Figure 3. For similar mass loss rates these materials would raise the allowable shield temperatures to around 3500°C. While these vapor pressures are not directly comparable to the ACF material study, they do represent both the present limitation of low vapor pressure materials and the potential for new materials.

The ACF effort focused on quantifying candidate refractory carbide materials' ability to inhibit vapor mass loss, using only commercially-available material sources and their proprietary process. A limited variety of precursor materials were used. Process variations were tested to show their effect on the material samples and how different parameters could potentially be optimized. These process tests resulted in confirmation of the material structures needed to suppress the vapor pressure and maintain mechanical strength. Also "more likely" conclusions were made on precursor materials and potential design options.

ISP Material Requirements

The scope of the study was not to define the materials to be used in an ISP thermal shield, but to identify candidate materials that might be used, so that further developments could take place on the materials, processing, and testing capabilities. For the study, the following material properties goals were defined.

- **Lightweight UHT materials**: Refractory carbides with high melting points could function as a solar shield, but their high density made the use impracticable. ACF's material development yields a composite material in the density range of 2 g/cc to 5 g/cc with UHT performance. This material option is significantly better (lower density) than any other material presently available and has the potential for operating well above 3000°C. The density range for these ACF materials are similar to that developed for the SiC-coated C-C leading edge used on the Space Shuttle which operated at less than 2000°C.
- **Other Key Material Properties**: thin-layer fabrication, reasonable strength, some ductility, good manufacturability.
- **Less Important Properties**: thermal conductivity, optical properties. An important design consideration is that thermal properties, such as optical properties and thermal conductivity are very hard to measure above 1000°C. A practical shield design cannot be based on predicting exact performance from a system that cannot be tested. Therefore, a wide uncertainty range in the allowable thermal proprieties, and multiple analytical and test verification paths are needed to ensure performance.
- **Other important considerations**:
  - **Scaling**: Materials must have the capability for scaled manufacturing of large-area (meters x meters) sections.
  - **Joining**: Materials and composites must be capable of joining of large sections.
  - **Shield Design Flexibility**: Rigid structure, as on PSP, versus deployable (flexible fabric). Single versus multi-layer laminate.

ISP Material Development

ACF's patented Direct Conversion Process (DCP_{TM}) process enables unique combinations of "converted" materials to be manufactured with desired properties for use in solar heat shields and a wide variety of applications, not limited to engines, hypersonics, industrial refractories, power generation and armor. In addition to the UHT capability, the process provides other design benefits.

- The process produces defined and uniform properties across the material that can be controlled. Material and processing options exist to control the internal structure of the material and its properties. As an example, for a given UHT exposure, the evaporation rate and layer thickness can be adjusted to produce an acceptable "lifetime" for the design.
- The material internal structure remains "non-bonded" which ensures conformal preform properties as well as the ability to design a flexible material option.
- Processing changes are available to produce different optical properties in different parts of the system.
- The material includes oxidation resistance that, while not important for the ISP design, is important in atmospheric systems.

While the details of manufacturing both the precursor materials and final materials are proprietary, both play key roles in either strengthening or weakening the materials. Material manufacture and fabrication affect the micro and grain structure in ways that have considerable influences on the finished product. Material defects and residual stresses are two of the principal factors leading to the degradation of tensile strength. Also, the effect of reduced vaporization of all the species in the final material may also be a factor in strength retention.

Material Developmental Approach - Project Test Samples

During the study, ACF, developed a list of candidate materials and their processing steps that were reviewed each week for progress in meeting objectives, discussion of changes given any "new knowledge", and issues with processing. Some materials were dropped after literature data was found indicating lower temperature dissociation or other less desirable material properties. Others were added as lower vapor pressure materials were identified. Five candidate materials were identified that were compared against a standard, lower-temperature material previously developed by ACF. Precursor material design options were evaluated.

Coupon Fabrication

Using ACF's process reactor, ACF adapted their existing equipment to process the ISP coupon samples for testing. Processing travelers were used to track and identify each Group during processing. For consistency in the material formation, precursor materials with different internal characteristics were all processed concurrently. Some samples were made for resistance heat testing others for mechanical testing. Not all samples were fully fabricated and tested because it was necessary to stay within the project scope and funding limits. Some sample processing was stopped as results indicated additional trial runs would be required needing additional time and effort. Others were able to be prototyped, as determined by EDS/SEM, on the first run. With JHU/APL concurrence, ACF focused on one material to make samples in keeping with the objective to demonstrate vapor pressure suppression at UHT. During this effort ACF also identified and explored the design features required to maintain thermodynamic stability within the materials.

UHT Testing and Results

The project goal was to collect evidence on vapor pressure suppression of materials at UHT. The project demonstrated that UHT, low vapor pressures, for low-density materials could achieved for the time durations needed for a near-Sun heat shield. A key finding of the study is that are very few standardized U.S. facilities that can achieve the UHT temperatures (2500 K to 5000 K) needed to test the ACF materials. To support the project, ACF agreed to replicate the type of resistive heisting facilities that are described in the early literature on high temperature material research.

The test procedure developed for the conduct of this experiment included:

- Mounting the sample onto copper electrodes and checking for sample resistance as the current is increased.
- Evacuating the chamber containing the test sample by turbo-pumping to 10(-4) torr or better.
- With the system and sample stabilized for at least 60 minutes, electrical power was applied to the sample in incrementally while the surface temperature of the sample (brightness) was measured using a calibrated Disappearing Filament Pyrometer (D.F.P). D.F.P. uses a tungsten filament and is factory-calibrated against known material temperatures and emissivity at 534nm. This wavelength is less sensitive to changes in temperature than longer wavelengths.
- In this technique, a rheostat-controlled constant Direct Current (DC) power (battery) was applied to the tungsten filament. The DC current created resistance which heats the filament

until the filament “disappears.” As sample brightness increases, so does the surface temperature. ACF used three calibrated ranges for temperature using three optical filters with an upper-brightness measurement limit of 4000 K (3727°C).

- To arrive at the actual (true) sample surface temperature, the recorded reading is adjusted for sample emissivity which typically ranges from 0.1 to 1: T(actual) = T(measured) / emissivity. Since the D.F.P. is operator dependent, a general range of D.F.P readings may be precise to +/- 100 degrees with an accuracy (true temperature) dependent on the knowledge of the sample’s emissivity.
- Each material had a different value for temperature-dependent emissivity
- The fabrication process can also have a strong effect on spectral emissivity for various reasons such as: surface roughness, the presence of an external oxide, and stoichiometry.

In this project, early calculations indicated that 200 to 1000 watts of power would be sufficient to heat the filaments to temperatures above 3000 K. Over the course of the testing, improvements to the testing apparatus resulted in a capability to heat samples to temperatures above 3500°C. Post-test analyses were performed using ACF’s in-house CoXem SEM and EDS equipment.

The first tests were performed on known materials to establish a baseline for comparison. Efforts were made to determine the vapor pressure of these materials and their potential dwell-times at certain temperatures. In these tests, the facility vacuum pressure increases were attributed material vaporization. With repeated resistance testing of reference and new material samples, the temperature accuracy was conservatively estimated to be -300°C to +100°C for samples in the 3000°C to 3500°C range. This uncertainty range is between -10% to +3.3%.

After the electrical power was set to “zero” and the samples were allowed to rapidly cool, a section was taken from the heated, center-portion of the filament and was taken for SEM and EDS analyses. The post-test filament appearance was compared to the pre-test images, for changes in surface texture and internal structure.

Lifetime calculations include both the vaporization rate of the exposed material and the diffusion of other species from inside the material to the surface. Literature data was referenced on the reactivity, and diffusion and vaporization rates seen in other tests. Those data were consistent with the ACF results.

Mechanical Testing

Selected samples were analyzed for mechanical properties using a 4-point flexural test method following the ASTM C1341 Standard Test Method for Flexural Properties of Continuous Fiber-Reinforced Advanced Ceramic Composites. ACF used Test Geometry IIA, which uses a four-point loading system utilizing two force-application points equally spaced from their adjacent support points with a distance between force-application points of one half of the support span. This type of test can provide information on fiber pullout; flexural strength and strain; fracture strength and strain; modulus of elasticity; and, stress-strain curves.

The 4-point bend test was conducted at room temperature and consisted of three different varieties of samples. The samples had different compositions, different cure temperature stages, and variable distances between mounting holders. The dimensions of the samples and the bend rates were the same.

Summary of Mechanical Testing Results

- All samples exhibited fiber pullout.

- Some samples displayed ideal bend-test results with a clear modulus of elasticity, yield point, ultimate strength, and flexural strength. This Stress/Strain graph was more elastic than ceramic due to the processing stages being different than the other samples.
- Some samples displayed results that were more ceramic and less elastic with less clear modulus of elasticity, yield point, ultimate strength, and flexural strength.
- The differing results of the bend tests are due to the cure stages and the elements in the ceramic makeup. These two things will affect the elastic/ceramic behavior and the numeric results among the modulus of elasticity, yield point, ultimate strength, and flexural strength.

Conclusions

The project goal was to collect evidence on suppressing vapor pressure in materials at UHT. This result was achieved within the constraints of time and funding. The project tested several materials that had both low vapor pressures at UHT and low-densities. These materials can meet and exceed the original UHT and time goals of a near-Sun heat shield. The UHT test results define a path forward for additional material development and testing. Other refractory materials exist and would benefit form additional testing and development. Shield design options include flexible or rigid shields consisting of a single type material or layered with several different types having complementary properties.

Phase I Materials Conclusions

- The potential for light-weight, low-vapor pressure materials extends the current 2273 K (2000°C) upper-performance limit of carbon to very high temperatures.
- These new materials may retain mechanical strength to temperatures up to at least 3173 K (2900°C) and potentially much higher.
- The uniform nature of the material makes realistic life time estimates at UTC exposures more reliable.

Path Forward

The results of this Phase I project have demonstrated the potential for development of an entirely new class of materials with UHT capability. For future projects, additional materials work should be funded to study the following topics:

- Further development and testing of candidate materials selected for potential shield designs.
- Examination of the basic materials properties beyond the expected operating temperatures of a potential shield or support structure.
- Enhanced and accurate methods and systems for testing materials at UHT, particularly above and below 3773 K (3500°C).
- Expand the methods for resistive-heating of larger samples and samples.
- Scale-up, supply-chain, rapid manufacturing and quality-assurance of the proposed materials and composites.

From a solar shield design perspective, the following non-exhaustive issues should be considered:

- Scalability of the technology.
- Ability to test reasonably sized shield analogs.
- Ability to predict, and minimize, shield optical properties.
- Design options to join shield sections together reliably.

Other Potential Applications for UHT MC/C Materials

- **EDL Heat Shields**: Shield materials that are lightweight can be used either in rigid form as an outer shell, or a flexible system could enable compact, deployable design.
- **Heat Exchangers**: Fluid transfer tubes designed to handle very high pressures and high temperatures simultaneously are more efficient and compact.
- **Propulsion**: Un-cooled nozzles for rockets; reaction detonation and turbine engines.
- **UHT Fasteners**: Novel designs for use in advanced turbine engines for the attachment of flexible blankets. ACF was recently awarded an ONR SBIR Phase I project on this Topic.
- **Nuclear Materials**: Versions of UHT materials are radiation tolerant. ACF was recently awarded a NASA SBIR Phase I project related to nuclear thermal propulsion.
- **Hypersonic Thermal Protection Systems (TPS)**: Rigid or flexible CMC aeroshell designs and components for hypersonic flight vehicles.
- **Flexible TPS**: Knitted 3D UHT fibers can be reinforced with short, chopped fibers and a flexible felt or woven 2D or 3D structures. This TPS can be shaped in advance but has the flexibility to conform to complex shapes which allows designs with reduce joints and seams.
- **Hypersonic Gap Fillers**: ACF UHT materials candidate for flexible filler with a high decomposition temperature and low char-yield (comparable to phenolic) and a high (>1%) strain-to-failure.