OXIDATION RESISTANT HfC-TaC ROCKET THRUSTER FOR HIGH PERFORMANCE PROPELLANTS

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SUMMARY

The purpose of this reasearch effort was to develop high temperature, oxidation resistant thrusters which would lessen the thruster cooling requirements, resulting in increased performance and longer life for onboard propulsion systems for spacecraft. This research effort focussed on developing ceramic matrix composites (CMCs) for this application, and specifically investigated the use of HfC stabilized with TaC. This material composition can potentially operate in a stoichiometric oxygen to hydrogen ratio at a temperature of 5000°F (2760°C) in a radiatively cooled mode.

Various compositions of HfC and TaC were deposited by chemical vapor deposition (CVD) and tested, in an attempt to identify the composition which offered the best oxidation resistance. Although it was identified that small amounts of TaC appeared to offer improved oxidation resistance over HfC alone, an optimal composition was not identified. A 25lbf thruster was fabricated from a novel CMC sandwich construction with a HfC-TaC matrix, and survived two test firings, each of 5 seconds before a failure in the injector caused the run to be aborted.

It was not possible to control the relative stoichiometry of the HfC and TaC composition throughout the reactor due to the large difference in the thermodynamics of the HfC and TaC formation from their respective chlorides. This also resulted in an inability to infiltrate TaC into the preform under the experimental conditions investigated. Other material compositions were fabricated and tested and two material systems; HfC-SiC functionally graded to $C_{(f)}$ /C and Re functionally graded to $C_{(f)}$ /C were selected for further testing.

These functionally graded composites have use in a number of propulsion applications presently of interest to NASA and the defense industry. Their ability to withstand extremely hostile thermal environments and the light-weight and high-strength exhibited from the $C_{(f)}$ /C composite make these materials particularly suited for these applications. In the Phase III which is presently underway, Re functionally graded to $C_{(f)}$ /C is being further developed and tested for application in the thrust cells for the Linear Aerospike Engine for the X33 and RLV.

I. INTRODUCTION

The purpose of this research effort was to develop high temperature, oxidation resistant thrusters which would lessen the thruster cooling requirements and result in increased performance and longer life for on-board propulsion systems for spacecraft. At the time of this original research effort, rocket engine manufacturers were looking at improving the performance of satellite propulsion systems through increased chamber pressures and temperatures and by increasing the nozzle expansion ratios to produce specific impulses of 320 to 326 seconds using earth storable liquid bi-propellants such as N_2O_4/MMH and N_2O_4/N_2H_4. The proposed thruster is based on a HfC-TaC refractory matrix ceramic matrix composite (CMC), which can potentially work in a stoichiometric hydrogen to oxygen ratio and at a temperature of 5000°F (2760°C) in a radiation cooled mode. The excellent oxidation resistance and thermal stability will result in improved specific impulse, reduced mass and a substantially longer service life than is capable with the present metal thruster technology.

Conventional thruster materials used in low thrust, bi-propellant rockets consist of niobium alloy (C-103) coated with a fused silica (R-512A or R-512E) for oxidation protection. The chamber life is limited by degradation of the oxidation resistant coating which, following thermal cycling, cracks and spalls due to the difference in coefficient of thermal expansion (CTE) between it and the base metal. In order to maintain a thermally stable protective coating the use temperature must be limited to below approximately 2912 °F (1600°C) by the use of film cooling with uncombusted fuel. When operating at a temperature of 2550°F (1400 °C), the chamber life is only approximately 10 hours.

The next generation of thrusters with improved performance are based on rhenium with an iridium coating to provide adequate oxidation resistance. These thrusters have shown exceptional performance, operating at 4000°F (2200°C) for a total life of over 17 hours, using MMH/NTO liquid propellants. With time, however, the rhenium diffuses into the protective iridium coating, thereby reducing the oxidation resistance. The expense of manufacturing theses thrusters and their weight are undesirable, but their superior performance compared to conventional niobium thrusters has justified continued development.

The development of future high temperature propulsion thrusters requires the combination of both more severe combustion conditions (temperature and pressure) in order to improve the specific impulse and significant weight and cost reductions. The proposed functionally graded CMC thruster utilizes the exceptional properties of a solid solution of HfC-TaC on the interior surface which is exposed to the severe oxidizing conditions, functionally graded to a carbon matrix on the outer surface of the CMC thruster. This combination provides exceptional oxidation resistance at a reduced weight and cost.

The HfC-TaC system should withstand the extremely high wall temperatures which arise during the uncooled combustion of propellant-oxidant combinations such as H/O, MMH/N_2O_4 and ClF_5/CH_4, thereby allowing these thrusters to be radiation cooled. In terms of satellite propulsion system requirements, the proposed HfC/TaC composites offer three major payoffs:

1. Improved specific impulse
2. Reduced inert mass
3. Substantially longer service life

Higher specific impulse results in longer satellite station keeping and therefore an extension in the usable life of communication, earth sensing and astronomical satellites. For deep space probes, the propellant mass required to achieve a mission such as Galileo is traded against probe mission capabilities and longevity during the experimental vehicle design process. The use of refractory carbide composite thrusters shifts the design trade in favor of additional mission capability. In the case of low earth orbit space platforms, such as Space Station, higher efficiency translates into substantial savings on routine costs because less expendable propellant has to be boosted to orbit.

The use of advanced refractory CMCs for propulsion thrusters appears to be key to meeting many of the Integrated High Payoff Rocket Propulsion Technology (IHPRPT) initiatives whose goal is to double rocket propulsion capability and reduce hardware costs by one fifth by the year 2010. As thruster propulsion technology evolves it is evident that these goals will only be met through the use and containment of higher energy fuels, and higher combustion pressures and wall temperatures, and that light-weight materials are essential in their containment.

The overall objectives of this research effort were to:

1. Improve the oxidation resistance of the HfC-TaC refractory system.
2. Build a material database including high temperature properties for the HfC-TaC CMC system.
3. Design, fabricate and test thrusters based on the optimum HfC-TaC composition.

These objectives were expected to develop a materials system and to extend the processing knowledge to a commercial payoff through the interaction with end users. What follows is a detailed summary of the phase I and II research.

I.1 Rationale on the HfC-TaC Composition

The service life of radiatively cooled HfC or HfC-TaC rocket thrusters is dependent ultimately on the kinetics (rate) of the oxide scale formation and its protective qualities. The literature presents conflicting data on the oxidation characteristics of HfC and HfC-TaC compositions. The following discussion highlights the key differences in these data and provides the background rationale for the composition optimization studies outlined in this proposal.

HfC will be oxidized to form hafnium oxide (HfO_2) which is one of the most stable refractory compounds. Hafnium carbide has a melting point of 5252 °F (2900°C). HfO_2 in the pure form crystallizes in the monoclinic phase at room temperature but transforms into the tetragonal phase over a temperature range of 2900°F - 3182°F (1600-1750°C), becoming fully tetragonal above 3182°F (1750°C). On cooling, the tetragonal phase transforms back into the monoclinic phase. A large volume change of approximately 3.4% is associated with this transformation, a characteristic that can cause structural degradation under repetitive thermal cycling. The vapor pressure of HfO_2 at 4832°F (2667°C) is about $3x10^{-5}$atm, making it the least volatile of all the oxides even though its melting point is several hundred degrees below that of thorium oxide[1].

Refractory Composites Inc., (RCI), CCI's predecessor, had previously reported on the rather peculiar oxidation behavior of the HfC system. At temperatures below 3000°F (1650°C) and as low as 900°F (480°C), a runaway oxidation phenomena is observed in this system. This phenomenon is known as pesting. An oxide scale grows in the carbide until it reaches a critical thickness, spalls and exposes fresh carbide to further oxidation. The monoclinic-tetragonal phase transformation probably exacerbates this phenomenon. Parabolic protective oxidation behavior is thus short circuited and high oxidation rates are observed. Above 3000°F (1650°C) the oxide scale does not rupture and parabolic oxidation (desirable) behavior is observed. In the rocket thrusters application, the surface temperature of the skirt drops below 3000°F (1650°C) as the propellants expand through the exit cone. This temperature is based on an area ratio of 10 that produces a 2000°F (1100°C) plus drop in temperature from the 5000°F (2760°C) flame temperature conditions.

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[1] For review of properties of hafnium carbide and hafnium oxide, see the following:
Storms, E.K., **The Refractory Carbides**, Academic Press, New York, London, (1967).
Toth, L.E., **Transition Metal Carbides and Nitrides**, Academic Press, New York, London, (1971).
Alper, A.M., **High Temperature Oxides**, Academic Press, New York, London, (1970).
Perry, A.J., "The refractories HfC and HfN - A survey I," Powder Metall. Int., **19**, No. 1, 29 (1987).
Perry, A.J., "The refractories HfC and HfN - A survey II," Powder Metall. Int., **19**, No. 2, 32 (1987).
Galasso, F.S., **Chemical Vapor Deposited Materials**, CRC Press, Boca Raton, Boston, London, (1991).
Courtright, E.L., et al. "Ultrahigh temperature assessment study - Ceramic matrix composites," WL-TR-91-4061, (1992).

I.2 Hf-Ta Alloy Protective Oxide Films

The expectation of better oxidation protection of an oxide scale that forms from HfC mixed with TaC is inspired by the high temperature oxidation behavior of Hafnium-Tantalum alloys[2]. Oxidation studies on the Hf-Ta metallic alloy system have shown that hafnium alloy with 27 wt% tantalum provided the maximum oxide film protection over the temperature range of 3000-4000°F (1650-2200°C). The oxide-reaction zone thickness reached a minimum thickness at 4000°F.

The unique oxidation resistance of the Hf-Ta alloy system is related to the stabilization of the high-temperature tetragonal phase of HfO_2 by one or more phases of tantalum oxides. A resulting dense, tenacious, and crack-resistant oxide film significantly reduced the amount of oxygen diffusing through the oxide. Metal rich tantalum stringers in an ordered Widmannstatten pattern provided an interlayer attachment (adherence) mechanism between the bulk carbide and the tetragonal HfO_2 surface layer. In addition, tantalum oxide, a glass-forming oxide with very low vapor pressure, could provide a resealing mechanism to help heal a cracked or ruptured oxide layer. The amount of Ta was critical as maximum oxidation resistance was reached with 27 wt.% Ta addition. Too little tantalum in the base alloy resulted in a mixed tetragonal-monoclinic hafnium oxide, while too much tantalum produced an excess of the lower melting tantalum oxide phase.

I.3 HfC and HfC-TaC oxide Films

The oxidation resistant properties of hafnium carbide could show a significant improvement, if the same benefits found in the Hf-Ta alloy system could be derived in oxide scales formed form the HfC-TaC system. The one oxidation study of HfC-25TaC system found in the literature revealed parabolic oxidation behavior for 90% dense bulk hot-pressed samples oxidized at isotherms form 1200°C to 2200°C. Above 1900°C, the oxide layer was a mixture of HfO_2 and $Hf_6Ta_2O_{19}$ and heavily cracked throughout its entire thickness[3]. No evidence of the Ta metal stringers that anchor the HfO_2 to the Hf-Ta alloy substrate was seen.

CCI is of the opinion that CVD or CVI HfC-TaC microstructures will not exhibit the same deleterious oxidation behavior. This is based on the results of a recent high temperature oxidation investigation of CVD deposited HfC films by Bargeron and Benson[4]. Substoichiometric $HfC_{0.5}$ (face centered cubic) films with a grain size distribution between 10µm and 100µm formed continuous, adherent hafnium oxide films below (1400°C) and above (2060°C), the hafnium oxide monoclinic to tetragonal phase transformation temperature, respectively. Both films displayed an intermediate hafnium oxycarbide phase with a distinct boundary (indicative of bulk diffusion) at the carbide interface.

Oxide thickness formation as a function of time at 1400°C and 2060°C exhibited a parabolic rate, kinetics which are representative of protective oxide films. These parabolic oxidation-bulk diffusion results from CVD HfC films are in direct contradiction to the linear oxidation kinetics-grain boundary diffusion mechanism of arc-melted HfC specimens reported by Berkowitz-Muttuck[5]. The oxidation behavior of the CVD HfC films is far more attractive than the bulk hot-pressed or arc-melted HfC specimens. A parabolic rate constant determined from the 1400°C thickness-time plots predicted that the carbide would be completely oxidized in 700 hours. Obviously, structural integrity and leakage of the thruster would be comprised prior to complete oxidation of the carbide phase. These promising CVD results warrant a more in-depth study of the oxidation characteristics of the CVI HfC-TaC CMC system in order to determine the composition best suited for long life thruster performance.

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[2] Marnoch, K., "High temperature oxidation-resistant hafnium-tantalum alloys," J. Metals, 1225 (1965).

[3] Prater, J.T., "Modification of hafnium carbide for enhanced oxidation resistance through additions of tantalum and praseodymium," AFWAL-TR-88-4141 (1988).

[4] Bargeron, C.B., and Benson, R.C., "High temperature oxidation of hafnium carbide," Proc. of the 13th Conference on Metal Matrix, Carbon and Ceramic Matrix Composites, p.69, Cocoa Beach, FL, Jan. 1988. NASA CP-3054.

[5] Berkowitz-Muttuck, J., "Thermodynamic and Kinetic Studies for a Refractory Materials Program," ASD-TR-62-204 Part 3, April (1984).

II. SUMMARY OF PHASE I RESULTS

II.1 Materials Selection and Characterization

In the phase I research several compositions of different Hf/Ta ratios were deposited onto graphite substrates and characterized using X-ray diffraction (XRD). The compositions were then subjected to a series of oxidation treatments both at 1200°C and using an oxy-acetylene torch to determine their oxidation behavior and to identify a material composition with optimal performance. Selected samples were coated in a combination of glassy oxides by dipping in various sol compositions in order to enhance the oxidation protection.

Four different compositions of HfC-TaC were deposited onto graphite substrates as shown in Table I. The HfC and TaC materials were produced from the direct chlorination of Hf and Ta metals respectively at 750°C - 800°C, and their subsequent deposition in the presence of methane at approximately 1150°C. Each of the runs contained several graphite samples for subsequent XRD oxidation and sol coating/oxidation testing. The sol coatings which were applied to the as-deposited HfC-TaC coatings for added oxiadtion resistance were Al_2O_3 neutral pH, B_2O_3-SiO_2-Y_2O_3-ZrO_2 and SiO_2-Y_2O_3-ZrO_2, which were both acidic. Unfortunately, the sol coatings did not adhere well to the mixed HfC-TaC surfaces following drying and sintering at 1100°C and it was speculated that the degradation was due primarily to the large differences in coefficient of thermal expansion between the coating and the substrate and the large change in volume due to the dewatering and shrinkage of the sols during heating.

Table I. Processing Conditions for Hf-Ta Variations

	Run 1	Run 2	Run 3	Run 4
Hf/Ta Input Wt. Ratios	800/200	700/300	800/200	900/100
T (°C)	1150	1150	1150	1150
P (torr)	5	7.5	15	5
CH_4 (sccm)	100	100	100	100
Cl_2 (sccm)	200	400	400	400
Hf Burn Rate (g/h)	-	70	83	88
Ta Burn Rate (g/h)	7	30	18	12
Run Time (h)	6	6	6	6
Variation in deposit wt.	0.9 - 1.4	1.1 - 1.9	5.7 - 10.0	1.7 - 3.2

Samples of each of the HfC/TaC compositions were heat treated at temperatures between 1000°C and 1200°C for between 1 and 8 hours. At 1000°C the 80/20 sample formed an adherent white coating identified as HfO_2 and Ta_2O_3 which lasted well over the 8 hour period and appeared to offer protection. The 70/30 sample, with time, formed an oxide coating which flaked away being replaced by another oxide layer. The 90/10 sample behaved in a similar fashion to the 70/30. At 1200°C similar oxidation behavior was observed although the 90/10 oxide film appeared most uniform and the 80/20 oxide film did not perform well.

The four composition samples were also tested using an O_2/C_2H_2 torch with a 4:1 O_2/C_2H_2 ratio for 5 minutes. An optical pyrometer was used to monitor temperature during the tests; the temperature range was 2500 - 3000°F. In order to imitate the firing of the thruster, a rapid heat up was performed and the flame was traversed across the sample for uniform heating.

The solcoated and uncoated 80/20 samples both degraded during the test. The overcoat sample had small pieces of coating spall off the sample for about 3 minutes until bare graphite remained. The uncoated 80/20 samples appeared to heat uniformly and protected the graphite substrate for the first 2 minutes of the test. The complete coating spalled off the sample at that point, resulting in catastrophic oxidation. This coating, which was not ruled out by the oxidation testing, was dropped from consideration following this test.

The 70/30 film held up well during the 5 minute test. Some sparkles were observed on the coating, which is attributed to non-uniformities in the composition. The resulting sample had a white, nearly continuous glaze over the surface. X-ray diffraction analysis, shown later, indicated that a mixed HfO_2-Ta_2O_5 layer was present. The 90/10 film also looked uniform throughout the test. No sparkles were observed; the final appearance was smooth. The coloration of the final coating was puzzling; the heated surface was black, however, there was a white oxide coating along the sides of the samples.

II.2 Thruster Fabrication

In the phase I research, a 25lbf thruster was fabricated and densified using the 70/30 (HfC/TaC ratio) which performed best in the coupon testing. The thruster design was unique in that it was braided and densified by CVI twice, producing a sandwich type structure approximately 3mm thick. The initial braid was overcoated with a 100μm layer of HfC/TaC before being braided and densified again.

Following densification, the thruster was hot-fired at NASA Lewis using O_2/H_2 propellants. Two firings were carried out on the same thruster and a thrust chamber pressure between 65 and 75psi was maintained even though the overall composite density was less than 60%. The novel composite sandwich construction which contained an internal impervious layer of HfC allowed these pressures to be maintained throughout the tests even though the bulk of the fiber compsite contained open porosity. A hydrogen/oxygen gas mixture of approximately 6.5 resulted in an adiabatic flame temperature of approximately 3250°F (1789°C). An outer wall temperature of approximately 2635°F (1450°C), was measured during both tests. The thruster performed well although a slight drop in pressure (down to 64 psi) was measured during the second test.

Following hot firing, the thruster was sectioned and analyzed to observe the microstructure and damage due to firing. Sections were taken from the combustion chamber the neck and from the exit cone. Analysis was carried out in an Hitachi S800, Field Emission, Scanning Electron Microscope (FESEM). The elemental content of the "dense layers" and the infiltrated fiber layers were analyzed using a Tractor Northern 5500 energy dispersive X-ray analyzer (EDXA), which was attached to the FESEM.

All three sections, in general, appeared to show the same microstructures except for the absence of the inner dense layer in the throat section. The dense layer appeared relatively dense and continuous on the outer and middle layers, but was porous and severely eroded (where visible) on the inner layer. A section through the thruster is shown in Figure 1 and clearly shows the sandwich-type construction and the erosion of the inner dense layer of HfC in the throat region. Elemental compositions revealed that although HfC was found everywhere the presence of Ta was foaund only in the densely coated sections and then only a small amount estimated at being below 10% by wt. The inner dense layer was only present in the regions away form the neck and in these regions it was porous, severely eroded and contained no Ta.

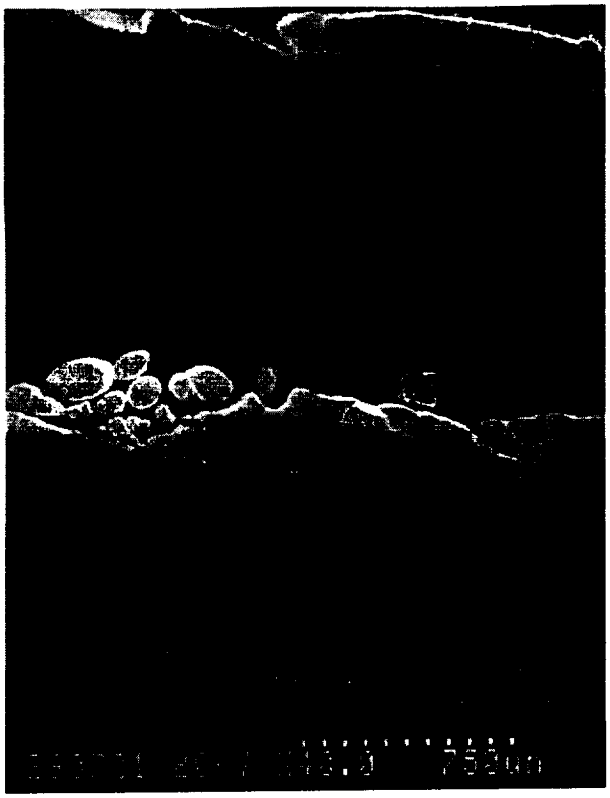

Fig. 1. Electron micrograph of the thruster cross section revealing the dense layers of the novel sandwich construction on the outer and middle sections. The inner section was contaminated.

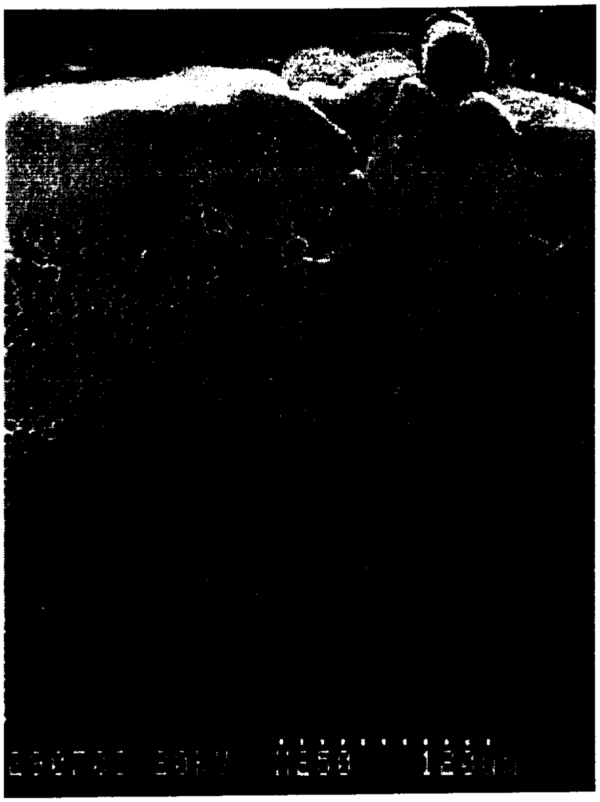

Fig. 2. Region near the surface of the thruster showing individually coated fibers and the well bonded surface coating of HfC.

The coating of the individually braided fibers can be seen to be graded from an occasionally heavy coating on the outer fibers of the exposed bundle (about 3µm thick), to a discontinuous coating of 0.1µm nodules. On most of the fibers, the coating whilst nodular in appearance was continuous and was between 0.2µm and 0.5µm thick, as shown in Figure 2. EDXA analysis of this coating revealed only Hf.

In summary we can see that infiltration of the fiber bundles ranged from "good" to "poor" and that no Ta was deposited in the bundles. The dense sealant layers on the outer and middle sections appeared dense and relatively continuous, and contained small amounts of Ta (typically less than 10% by wt.). The (originally dense) inner layer had been almost completely eroded from the neck section and was porous and severely eroded in the other two sections.

III. SUMMARY OF PHASE II EXPERIMENTAL PROCEDURE AND RESULTS

III. 1. Introduction

The phase II research effort focused on a series of experiments which evolved in an effort to find suitable deposition conditions for the HfC-TaC solid solution.

Following analysis of the phase I thrust cell, it was determined that there were problems in controlling the HfC-TaC codeposit composition. Initial tests focused on ways to control the HfC-TaC composition within the preform and as coatings. Experiments followed to produce controlled HfC-TaC stoichiometry in the vertical direction but these too were unsuccessful. Laminated HfC/TaC alternate layers were produced and annealed to form a solid solution. Particles of TaC were also distributed throughout the fiber preform and a matrix of HfC deposited around the particles by CVI.

Selected samples were subjected to static oxidation testing and the HfC-TaC ratio in each of these samples was determined by X-ray diffraction.

Finally a series of discs were produced containing an oxidation resistant interior section on a C/C composite. These discs were approximately 4 " in diameter and contained an interior hole onto which the oxidation resistant coating was applied suitable for testing at NASA Glenn. Four discs containing HfC/SiC coatings and two containing Re graded to C/C were supplied to NASA Glenn. In addition a 25lb$_f$ C/C thruster functionally graded to a Re interior was produced and supplied to NASA Glenn for testing. These components were considered as the Phase II deliverables.

III. 2. Understanding the HfC-TaC Codeposition Behavior

III. 2a. Experimental Approach

In the phase II research effort, analysis of the composition of the thrust chamber identified a significant difference between the HfC/TaC compositions on the as-deposited graphite substrates and between the infiltrated fiber preforms. The initial phase II research effort focused on controlling the HfC/TaC composition both in the coating and infiltrated fiber preforms. Controlled tests were carried out using the conditions described in table II to identify the key issues associated with the co-deposits of these materials and critical processing variables which affected this deposition.

Table II.
Summary of Processing Variables Investigated

Material System Chlorinated	Pressure (torr)	Temp. (°C)	Gas Combustion	Deposit
Ta	100 - 10	1125	normal	Ta, Ta_2C and TaC
Hf	100 - 10	1125	normal	HfC
Hf - 30%Ta	100 - 10	1125	normal and with He replacing Ar	Ta, Ta_2C, TaC and HfC
Hf - 5%Ta	10 - 2	1125	He and CH_4 to 500sccm	Ta_2C, TaC and HfC
Hf - 5%Ta	5 - 2	1275 - 950	He and CH_4 to 500sccm	Ta_2C, TaC, HfC and C

Five carbon discs were arranged radially on porous graphite plate at each of three levels in the reactor. Gas entered the reactor through a small 2" diameter hole centrally located approximately 4.5" above the position of the first plate. Experimental parameters which were changed are summarized in table III below. Four major processing variables (material system, pressure, gas composition and temperature), were systematically changed and the radial composition at each of the three heights within the reactor was analyzed by X-ray diffraction and/or microstructural analysis by sectioning, polishing, and SEM observations. The results identified systematic differences and similarities between each experiment which has given us a better understanding of the critical deposition parameters.

III. 2b. Results

The results from each of these experiments clearly showed significant differences between the thermodynamics of formation of the Ta and Hf carbides. This was not unknown, but it was surprising that the target composition of HfC and TaC in solid solution could not be obtained over a larger volume considering the significant changes which were made to the processing conditions. At the top of the reactor the deposition rate was significantly higher than elsewhere. For all three levels the deposition rate dropped off slightly in the radial direction. Figure 3 shows a typical deposition rate as measured by the weight increase on the graphite discs versus radial position for a given set of conditions at 1125°C. Since the actual thickness was dependent upon the processing conditions and time, this graph is shown in relative amounts.

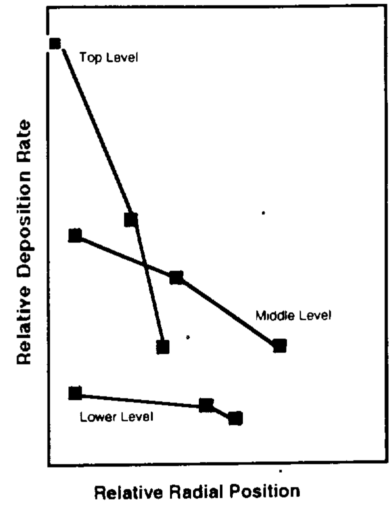

Figure 3. Graph Showing the Relative Deposition Rate Radial Position From Center

In all the tests where Hf was present, HfC was identified in all three levels of the reactor. Figure 4 shows the calculated yield for HfC (based on thermodynamics), for the processing conditions typically used, and demonstrates a yield of approximately 15% at 1125°C. This is in keeping with the experimental evidence which showed that at 1125°C, a considerable amount of $HfCl_x$ passes through the reactor without depositing in the hot region and eventually condenses and accumulates in the exhaust piping. As we go to higher temperatures the yield is improved but is still only 35% at approximately 1275°C.

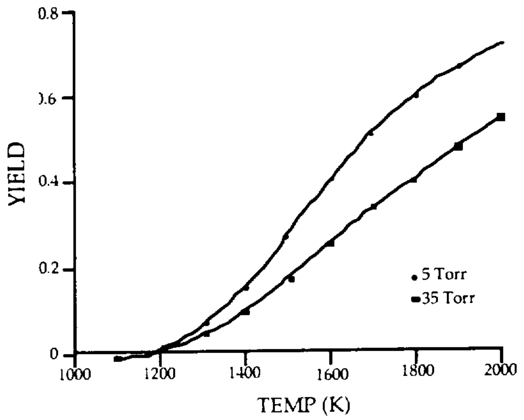

Figure 4. Graph Showing the Relative Yield for HfC versus Temperature

In the tests where Ta was chlorinated we see that there is a tendency for Ta compounds to deposit on the first hot surface which is encountered and often on the exit of the chlorination tubes. Although the CH_4 to Cl_2 ratio was initially suitable for HfC deposition, under these conditions it was found that $TaCl_x$ typically deposited as Ta metal or Ta_2C. In order to primarily deposit TaC it was necessary to increase the CH_4 to Cl_2 ratio 5 times. Under these conditions HfC was still deposited although the stoichiometry of the deposits have not yet been confirmed. The yield for TaC (based on thermodynamics) for the processing conditions typically used shows a yield of approximately 100% over the complete temperature range.

At lower temperatures there is a tendency for carbon to deposit and it was confirmed that our initial choice of temperature (namely 1125°C) was fairly good from the point of deposited single phases of Hf and Ta carbides. With the present reactor design we are able to deposit HfC-27wt%TaC at the first hot surface in the reactor using a Hf/Ta ratio consisting of 5wt% Ta.

III. 2c. Discussion and Relevance of Results

The results from each of these experiments show that the thermodynamic yields for the HfC and the TaC are very different. Firstly, at 1100°C the HfC yield is very low (~15%) and only increases to approximately 35% at 1275°C. The tendency for HfC is therefore to deposit fairly uniformly from the top of the reactor to the bottom. The yield for TaC however appears to be 100% over the complete temperature range studied (950°C to 1275°C). The tendency for TaC is therefore to deposit on the first hot surface which is encountered. Lowering the temperature down to 950°C appeared not to affect the kinetics of this reaction (which may have helped expand this TaC deposition region), and had the detrimental effect of depositing elemental carbon.

A summary of these initial findings concluded that with the present reactor design there were no processing conditions which could be selected to achieve deposition of the target composition uniformly in either the radial or axial directions. A decision was made to change the reactor design to incorporate a gas manifold which would deliver the reactive metal chlorides at a uniform concentration in the vertical direction. It was felt that by rotating the fiber preform (cylinder) about the axial direction it would be possible to coat the complete vertical height with the same composition.

III. 3. Attempts to produce uniform deposits in the vertical direction

In the preliminary tests which were conducted to investigate the idea of manifolding the reactive metal chloride gases directly onto the manifold it was quickly realized that this approach led to heavy deposits at the exit of the manifold and that very little material could be deposited onto the fiber preform/mandrel in this way. In addition the Ta in particular was depleted from the chloride gas stream leaving only Hf available for deposition/infiltration.

III. 3a. Experimental Approach

In an effort to coat the fiber preform uniformly and to maintain the HfC-TaC stoichiometry in the vertical direction, the regular set-up shown in Figure 5i was changed to a manifolded system, as shown in Figure 5ii, where the reactive gas stream is fed onto the fiber preform through a narrow slit running the complete height of the preform.

III. 3b. Results

In the regular set-up illustrated in Figure 5i, Ta species are quickly deposited onto the top of the preform as shown. In many cases Ta metal will deposit out first, followed by Ta_2C and TaC further down the preform. After a short distance however the Ta is depleted from the gas stream irrespective of whether Hf species are present or not. The deposits which are obtained from the manifold system also show a propensity for Ta species to deposit at the top of the fiber preform, as shown in Figure 5ii. Excessive discoloration/deposit also occurred on the manifold which was fabricated from quartz.

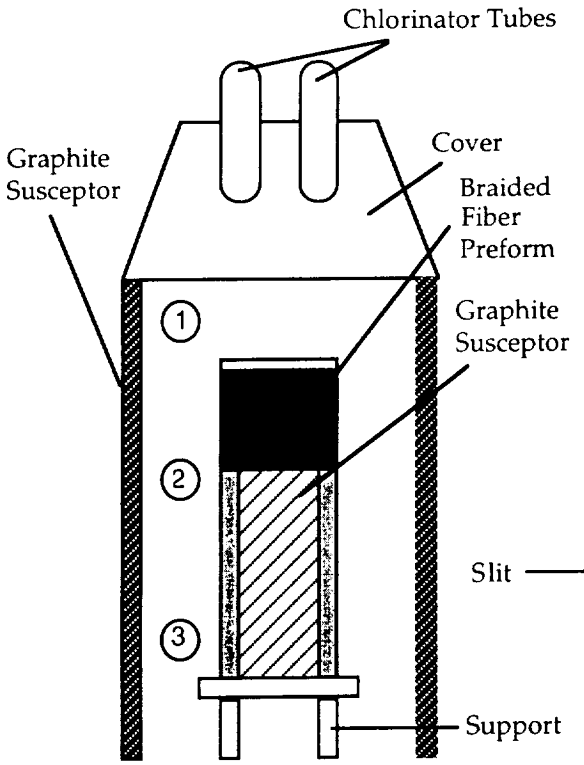

Figure 5i. CVI/CVD experimental setup for isothermal deposition of HfC/TaC mixtures.

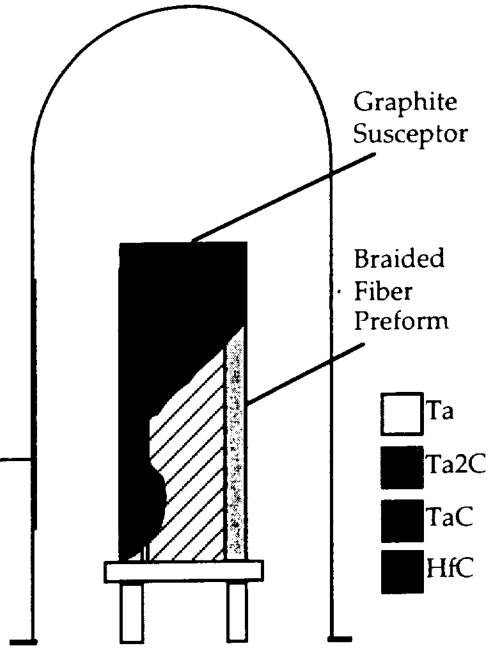

Figure 5ii. Altered experimental setup showing the position of the slit through which gas enters the bell jar, which surrounds the workpiece.

III. 3c. Discussion and Relevance of results

These results show that it is very difficult to control the deposition of TaC and that it is therefore difficult to control the HfC-TaC stoichiometry. The Ta species have a tendency to deposit quickly from the gas stream onto the first hot surface they encounter. In this experiment, even the quartz manifold became hot enough that Ta deposition occurred on it.

III. 4. Summary of the Phase II Deposition Studies after 15 months

In summary, the results from each of these experiments show that the thermodynamic yields for the HfC and the TaC are very different. Firstly, at 1100°C, the yield is very low (~15%) and only increases to approximately 35% at 1275°C. The tendency for HfC is therefore to deposit fairly uniformly from the top of the reactor to the bottom. The yield for TaC, however, appears to be 100% over the complete temperature range studied (900°C to 1275°C). The tendency for TaC is therefore to deposit on the first hot surface which is encountered. Lowering the temperature down to 900°C (which may have helped expand this TaC deposition region), appeared not to affect the kinetics of this reaction and had the detrimental effect of depositing elemental carbon.

The summary of these fundamental experiments has shown that with either the present reactor design or the modified cross flow reactor it has not been possible to change the processing conditions to achieve the target composition over a larger volume. The deposition characteristics of HfC and TaC are so different that it is not possible to deposit them either by CVD, or infiltrate a fiber preform by CVI and ensure the same $HfC\text{-}TaC_{(ss)}$ composition over an area of more than a few square inches. Although lamination of the HfC and TaC layers can be easily achieved and annealed to form a solid solution following 2 hours at 1600°C, once again it is not possible to control the layer thickness of the TaC within the laminate which varies depending upon its position within the reactor.

IV. ALTERNATIVE PHASE II RESEARCH PLAN

Phase II results on chemical vapor infiltration (CVI) of the oxidation resistant HfC-TaC solid solution system have demonstrated that due to the considerable difference between the relative stability of the Hf and Ta chlorides, it is not possible to deposit these materials simultaneously while maintaining control over the composition. It has also been shown that under a wide range of processing conditions, it is not possible to form a TaC matrix around a fiber preform due to the fact that the Ta chloride will not infiltrate into the preform. These results indicate that it is not possible to fulfill the initial tasks outlined in the Phase II proposal, requiring the fabrication of a carbon fiber reinforced HfC matrix thruster which contained approximately 30wt% TaC.

In light of these results, an alternative plan was outlined and submitted to Brian Reed in March, 1997. This alternative plan focused on the use of CCI's rapid RTG CVI process for the fabrication of oxidation resistant HfC based systems. Particular attention is being paid to the HfC-SiC system and to increasing HfC infiltration potential and CMC component density through nano-particulate infiltration into the carbon fiber preform prior to CVI matrix densification. Based on the most promising processing techniques and CMC architectures, CMC thrusters will be fabricated and evaluated for divert thruster applications.

IV. 1. Laminated HfC/TaC Matrix Composites

With the gas pulsing set-up presently available at CCI it is possible to switch between one gaseous precursor and another, thereby allowing alternate materials to be grown in discrete layers. In the past this approach has been used to produce alminated matrices with a variety of material combinations which showed improved toughness due to the matrix lamination. This approach has shown to be capable of producing laminates at sub micron scales up to several hundreds of microns in thickness.

IV. 1a. Results

Laying down alternate layers of HfC and TaC has been shown to be a good approach to achieveing control of the relative Hf and Ta concentrations in coatings over small areas. Infiltration of these layers however is not possible using chloride precursors since the Ta deposits on the outside of the fiber preform sealing off the internal porosity. A carbon layer was introduced between some of the HfC and TaC layers so that the thickness of the individual deposits of 7µm layers of HfC and TaC separated with a thin layer of carbon. Each of the HfC and TaC layers was deposited in a 7 minute period and the carbon was deposited in a 15 minute period using the ususal processing conditions. Figure 6 shows a fracture surface of a similar coating of only HfC and TaC 10µm and 7µm in thickness, respectively, revealing extremely large TaC grains compared with HfC. Once again this microstructure emphasizes the very different growth kinetics for TaC and HfC materials.

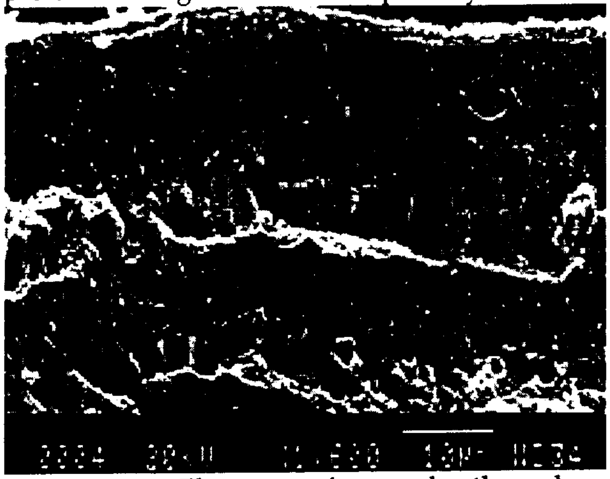

Figure 6. Electron micrograph through a laminated HfC/TaC multilayered coating. Notice the large columnar grain morphology of the TaC phase.

The thickness of the TaC layer varied depending upon the position within the reactor. It does not appear possible to control the stoichiometry of the HfC-TaC mixture over the area of the coating.

IV. 1b. Conclusions

Attempts to infiltrate both HfC and TaC simultaneously in a fiber preform resulted in no infiltration and a build-up of a thick surface coating of HfC and TaC. Laminated layers of alternate HfC, TaC and C (which acted as a visual marker) were successful, resulting in a trilayer thickness of approximately 7µm. It is possible that these layers can be annealed to produce a single phase $\text{HfC-TaC}_{(ss)}$ following 2 hours at 1600°C. Unfortunately, the TaC layer thickness depended upon the position within the reactor and so the stoichiometry of the $\text{HfC-TaC}_{(ss)}$ could not be controlled.

The results from HfC-TaC experiments demonstrated that the thermodynamic yields for the HfC and the TaC are very different. At 1100°C, the HfC yield is very low (~15%) and only increases to approximately 35% at 1275°C as shown previously in Figure 4. The tendency for HfC is therefore to deposit fairly uniformly from the temperature range studied (900 - 1275°C). The tendency for TaC is therefore to deposit on the first hot surface which is encountered. Lowering the temperature down to 900°C (which may have helped provide a more uniform deposit), had the detrimental effect of depositing elemental carbon.

IV.2 Static Oxidation Testing of HfC-TaC Specimens

Oxidation tests at ~1750°C were carried out on a number of different HfC-TaC compositions that were deposited by CVD onto graphite substrates. It has already been discussed that the HfC-TaC system cannot be effectively infiltrated into fiber preform via CVI. Thus, this oxidation testing was performed as a means to qualitatively determine the relative oxidation resistance of the HfC-TaC system as compared to HfC. Promising results would serve as rationale for CCI to explore alternative ways to fabricate the HfC-TaC system, such as through the introduction of TaC particles into the fiber cloth preform prior to CVI densification of an HfC matrix (annealing for 2 hours at 1600°C can produce a solid solution HfC-TaC system).

Oxidation testing was performed using an oxy-acetylene (O_2-C_2H_2) flame rig set-up. The HfC-TaC specimens tested ranged from 0%TaC to 22%TaC, as determined by X-ray diffraction analysis. A high O_2-C_2H_2 ratio was used to simulate strongly oxidizing conditions and the flame remained on between each test so that the conditions remained the same for each sample. The temperature of each specimen was determined using an optical pyrometer. The flame remained on each specimen for a total time of 10 seconds, the specimen was then removed and a new one was placed in the specimen holder for testing. The condition of the samples was determined by optical microscopy, weight change measurements, and X-ray diffraction. Oxidation would replace the carbon in the HfC with two oxygen atoms to form HfO_2, thus, a weight gain indicates oxidation. However, due to the CTE mismatch between the graphite substrate and the HfC-TaC coatings, significant spalling occurred on many of the samples, thereby negating the effectiveness of the weight change measurements.

IV. 2a Results

Table II shows the composition of all specimens that were tested and the results of the post-test analysis. *Although the results are very qualitative, and thus inconclusive, they do indicate a general trend towards more oxidation and more spalling with increasing TaC content.* The oxidation mass increase, mass increase per unit surface area, and mass increase per coating volume all indicate a trend toward more oxidation for the specimens with higher TaC content. Optical microscopy seemed to confirm this trend. The 0% TaC specimens showed relatively small amounts of the oxide phase on the surface, whereas Figure 7 is an optical micrograph of specimen #9 (6% TaC) that shows a lot of the white oxide phase on the surface of the specimen. Likewise, Figure 8 is an optical micrograph of specimen #17 (22%TaC) which shows a spalled section of the specimen where the coating has flaked off the corner. Post oxidation test X-ray diffraction analysis was inconclusive as all of the samples showed the major peaks for HfO_2 and HfC, and the specimens containing TaC also showed a small peak that indicates the presence of $Ta_{0.8}O_2$. *These results do not warrant the pursuit of other techniques, such as pre-CVI TaC particle infiltration, to process the HfC-TaC system.*

Table II. Specimen composition and oxidation test results

Spec. #	%TaC	Coating Mass, g*	Coating Surface Area, cm^2	Coating Thick-ness, cm**	Coating Volume, cm^3	Test Temp., °C	Pre-test Mass, g***	Post test Mass, g	Oxidation Mass Inc., g****	Mass Inc. per coating surface area, g/cm^2	Mass Inc. per coating volume, g/cm^3
1	0	-	6.33	-	-	1720	4.426	4.433	0.007	0.00112	-
2	0	-	5.83	0.020	0.118	1780	4.137	4.140	0.003	0.00051	0.025
3	0	1.555	4.71	0.026	0.122	1760	4.050	4.018	-	-	-
4	0	1.741	5.46	0.025	0.138	1730	3.624	3.628	0.004	0.00073	0.029
5	0	-	6.70	-	-	1760	5.313	5.068	-	-	-
6	0	-	5.71	-	-	1770	4.517	3.937	-	-	-
7	2	1.289	5.09	0.020	0.102	1750	3.709	3.715	-	-	-
8	3	1.747	4.59	0.030	0.138	1740	3.552	3.556	0.004	0.00087	0.029
9	6	1.760	5.33	0.026	0.139	1770	4.215	4.126	-	-	-
10	6	1.612	5.21	0.024	0.127	1770	4.140	4.145	0.005	0.00096	0.039
11	8	1.728	4.84	0.028	0.136	1790	4.343	4.365	-	-	-
12	10	-	5.71	0.023	0.131	1820	6.185	5.200	-	-	-
13	10	1.776	5.46	0.026	0.140	1790	4.146	4.151	0.005	0.00092	0.036
14	12	1.967	5.21	0.030	0.155	1810	4.656	4.337	-	-	-
15	14	2.045	5.58	0.029	0.161	1790	5.045	4.651	-	-	-
16	18	1.776	5.09	0.028	0.140	1800	4.354	4.360	0.006	0.0012	0.043
17	22	2.019	5.83	0.027	0.159	1790	5.470	4.548	-	-	-

* the coating mass of some samples could not be determined

**coating thickness was estimated from either the coating mass and surface area, or from direct measurement of spalled pieces; for some samples, the thickness could not be estimated be either technique

***the pre- and post-test masses are the masses of the sample (coating and substrate) prior to and after the oxidation test

****the samples for which no weight gain is listed are those that spalled significantly during testing and therefore showed a weight loss

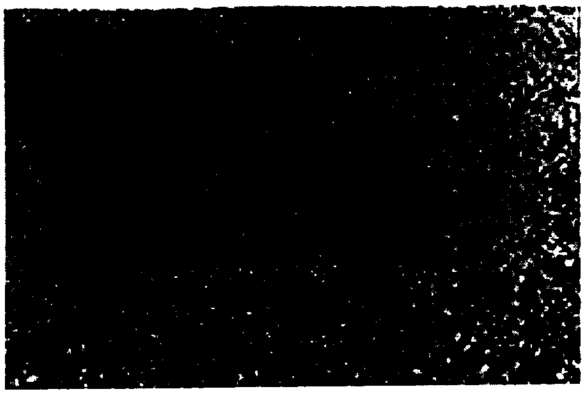

Figure 7. Post oxidation test optical micrograph of specimen #9 (oxide phase is white)

Figure 8. Post oxidation test optical micrograph of specimen #17 showing spalled corner

IV.3 Laminated HfC-SiC Multilayer Matrix Experimentation

CCI made a CVD deposit onto a graphite substrate of alternating C-SiC-HfC multilayers. Although extensive characterization of this deposit was not undertaken, the laminated material exhibited extreme toughness. In preparation for microscopic evaluation, the sample was very difficult to cut relative to other matrix systems with which CCI has experience. This led to further CVI studies where CCI looked at infiltrating an HfC-SiC laminated matrix into carbon fiber preforms. Figure 9 is a scanning electron micrograph of this system. Unfortunately, infiltration of the HfC phase into the fiber preform did not occur in a regular and controllable manner and HfC deposition primarily occurred near the surface of the preform. Also, the laminated HfC-SiC matrix deposit was not obtained in the CVI run due to the absence of the C layer, which served as a barrier between the deposition of the HfC and SiC phases in the CVD experiment. Without that barrier during the CVI run, the by-products of the SiC deposition may have precluded significant deposition of HfC, and/or vice versa. The C-HfC-SiC system did demonstrate potential properties that warrant further investigation. This will occur in the coming months and may lead to the use of that laminated system as a CVDed overcoat on the inside surface of the thrusters.

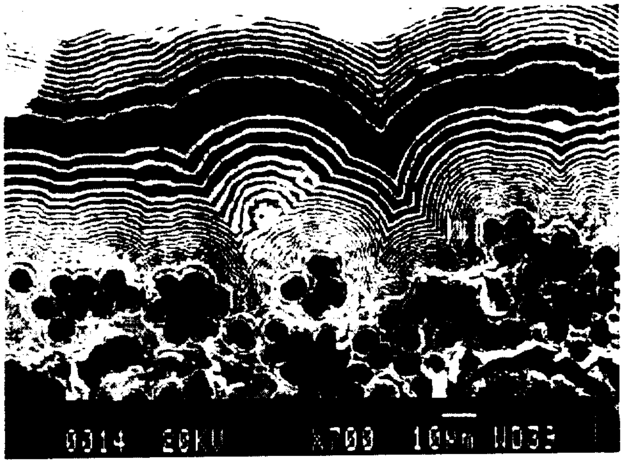

Figure 9. SEM micrograph of laminated HfC (light) and SiC (dark) matrix around carbon fibers

V. CHANGE IN THE PROJECTED SCOPE OF WORK

At this point in the contract, a discussion between NASA Lewis and Ceramic Composites resulted in a change in the materials focus of the program and in the allocation of remaining resources based on the results to date.

A subcontract with Kaiser Marquardt was involved and required a detailed chamber design based on the room and elevated temperature mechanical properties of HfC-TaC composites. The cost of the subcontract was to be $248,000 culminating in two 50 second tests of each of the thrusters. Since no mechanical property data was available and since it was unsure both how to produce a TaC/HfC solid solution matrix composite and whether or not the oxidation resistance of this material is superior to HfC alone, it was decided to carry out a more detailed materials evaluation of various HfC compositions with SiC, and to evaluate a new C-Re functionally graded composite which showed good results when tested at Thiokol.

In the final stages of this phase II research effort, samples were fabricated using the rapid CVI technique and sent to NASA Glenn for evaluation. Following a materials evaluation HfC/SiC and Re compositions were down selected to fabricate components for testing at NASA Glenn. Two sample shapes were made for materials evaluation testing using the gaseous H_2/O_2 flame rig, one in the shape of a 25lbf thruster and the other in the shape of a hollow puck. The puck shape was to simulate the throat region and to measure relative ablation rates, and the thruster was to simulate an actual thruster burn. Six pucks were fabricated, four of which had a HfC/SiC interior region and 2 of which were Re functionally graded to $C_{(f)}/C$ composite. The single thruster was triaxially braided carbon fiber, functionally graded from a carbon exterior to Re over the inner 30mils of the thruster wall.

V.1 Potential Application of the results and projected phase II activity

During the period which covered the phase I and II research efforts, it was established that while the HfC-TaC may offer additional oxidation resistance to systems containing HfC alone, the deposition kinetics for the HfC and TaC are very different and do not allow for control of the HfC:TaC ratio during deposition either in the radial or axial directions. Similarly, it has not been possible to identify suitable conditions which resulted in the infiltration of TaC into the fiber preform.

The phase II research effort, however, allowed for the fabrication of a wide range of advanced refractory composites, some based on HfC and others on Re, which have shown excellent oxidation resistance at elevated temperatures and which have allowed significant improvements in the processing of these materials to be achieved.

Present functionally graded composites based on refractory Re and mixed HfC-SiC systems have use in a number of propulsion applications that are presently of interest. The advantage of the HfC-SiC system over the Re system is its potential to perform well in strongly oxidizing environments, such as the propulsion thrusters in the Mars Ascent Vehicle, and in leading edges and turbine engine components in future hypersonic vehicles. The Re based composite system offers unprecedented performance in systems operating in high temperature, moist conditions, such as the Linear Aerospike thrust cells and ramp materials. A phase III program is presently underway to fabricate and test a functionally graded $C_{(f)}$-C/Re cryogenically cooled composite for the application in the Aerospike thrust cell.

V.2 Hf-C (solid phase) Infiltration Experiments

As discussed previously, uniform infiltration of a HfC matrix via CVI is difficult and has yet to be achieved. For unknown reasons, infiltration of the precursor reactive gases ($HfCl_2$ + methane) that form HfC does not readily occur. CCI personnel have noticed that the $HfCl_2$ gas will react with solid phase carbon to form HfC under the CVI processing conditions. This finding was confirmed by a thermodynamic analysis using the HSC Chemistry for Windows program, which demonstrated that the formation of HfC from vapor phase $HfCl_2$ and solid phase carbon is favored, particularly if the amount of excess Cl_2 can be minimized. Experiments were conducted to determine the feasibility of improving HfC matrix infiltration/densification into a carbon fiber preform by infiltrating the $HfCl_2$ vapor and reacting it with a solid phase carbon source previously infiltrated/deposited.

The initial experiment consisted of infiltrating/depositing alternating layers of carbon (methane reactive gas) and Hf ($HfCl_2$ reactive gas) to see if the $HfCl_2$ would in fact react with the previously infiltrated layer of solid phase carbon in order to form HfC. Hafnium metal was placed in a tube through which the chlorine gas entered the CVI chamber in order to form the $HfCl_2$ reactive gas. The introduction of the methane and $HfCl_2$ gases was alternated for 15 minutes each for a total run time of 6 hours. The run conditions are shown in table I. The results show that HfC was formed with excess layers of carbon. Figures 10 and 11 are SEM micrographs of this sample showing the bi-layer type structure. The thinner layer of each bi-layer is the excess carbon.

Table I. CVI run conditions for alternating Hf and C experiment

Temp.(°C)	Pressure	Ar flow rate	H_2 flow rate	$Ar_{\text{(chlorinator tube)}}$ flow rate	Methane flow rate	Cl_2 flow rate
1250	varied - chamber left open to vacuum	4 SLPM*	4 SLPM	100 SCCM**	400 SCCM	400 SCCM

* Standard liter per minute @ 1atm., 25°C
**Standard cubic centimeter per minute

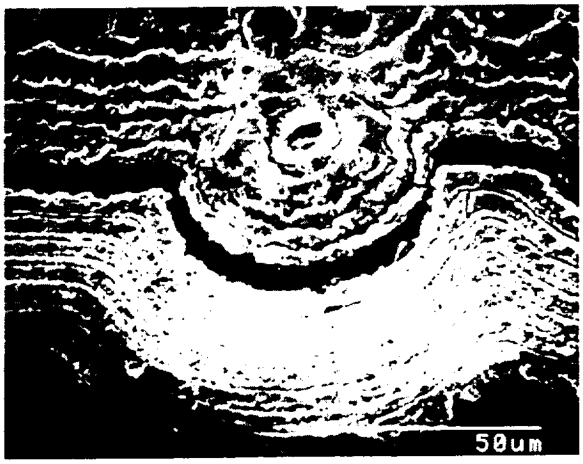

Figure 10. SEM micrograph of HfC matrix (with excess C) around C fibers

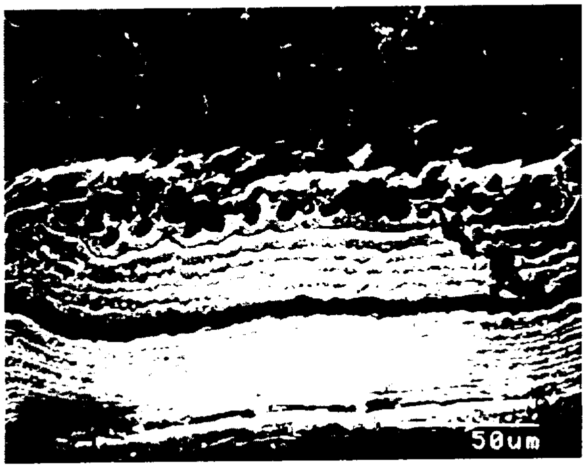

Figure 11. SEM micrograph of HfC matrix (with excess C) around C fibers

A second CVI experiment was performed to try to reduce the amount of excess carbon. The introduction of the methane and $HfCl_2$ gases was alternated; 15 minutes of $HfCl_2$ for every 1 minute of methane. The run conditions were the same as those for the previous experiment, as shown in table I, and the total run time was 6 hours. Once again, the HfC matrix showed excess carbon, though not as much as the previous experiment. Also, infiltration of the matrix was not very good. This can be seen in figure 11, which shows a good matrix deposit on the outside of the fiber bundles but not a lot of infiltration. For these reasons (excess carbon, poor infiltration), no further work was done on this process. However, CCI believes it is a process that should be further evaluated in later programs. HfC formation is favored and if the conditions can be optimized, then a breakthrough may be possible. Unfortunately, however, the process could not be further evaluated and optimized within the time frame of this Phase II program.

V.3 Pre-CVI Particle Infiltration

Research has been underway to develop a process to vacuum infiltrate particles (SiC, HfC, B_4C) into the carbon fiber preform prior to CVI. These particles are intended to fill the macropores in the C fiber preform and thereby create more surface area onto which deposition can readily occur during CVI. If optimized, this process can increase CMC component density while reducing processing time.

An experiment was conducted to look at infiltrating CCI's nano-SiC particles into the carbon fiber preform prior to CVI. The experiment evaluated three cylindrical carbon fiber preform samples (triaxially braided). The first was vacuum infiltrated with the sugar-sol (SiO_2) for three cycles (30 minutes per cycle). The sample was then placed in an inert atmosphere furnace at 1625°C for calcination of the sugar-sol to form the nano-SiC particles *in-situ* within the fiber preform.

The second sample was vacuum infiltrated (three 30 minute cycles) with a nano-SiC slurry and then dried. The slurry used to infiltrate the nano-SiC had a solids loading of 15vol% and contained ethanol as the infiltrating medium. The third sample was not subjected to any pre-CVI infiltration process. The three samples were simultaneously densified with a SiC matrix via an 18 hour CVI run. The mass of each sample was taken before and after the CVI run to get a qualitative feel for the densification efficiency. The results, shown in table II, show that the samples which were infiltrated with nano-SiC prior to CVI realized less SiC infiltration/deposition during the CVI process. This indicates that the particle infiltration process may be acting to block infiltration by clogging some of the open surface porosity.

Table II. Mass gain results of nano-SiC vacuum infiltration/CVI experiment

Sample #	Pre-CVI Treatment	Pre-CVI Mass (g)	Post-CVI Mass (g)	Mass Gain (g)
1	sol-sugar solution infiltrated - calcined	79.76	81.14	1.38
2	nano-SiC slurry infiltrated	67.09	69.26	2.17
3	none	69,7	73.21	3.51

A second experiment, run parallel with the above experiment, looked at a range of particle bed compositions and evaluated the infiltration of SiC by CVI throughout the particle beds. The particle beds were subjected to a 10 hour CVI densification run. Following CVI, the structural integrity of each was evaluated qualitatively prior to an oxidation test in which each sample was placed in an air furnace at 1400°C for 8 minutes. The pre- and post-oxidation test mass measurements were taken. Table III shows all particle bed compositions (bi-material compositions were 50:50 by weight%) and the oxidation test results. The results in table III are inconclusive because mass changes during oxidation could not be determined accurately due to spalling which occurred on some samples during the test. Based on the SiC CVI infiltration efficiency and the structural integrity of the samples following oxidation, it was determined that the HfC-B_4C and HfC-SiC powder bed compositions would be further evaluated. Larger samples were prepared for a range of compositions for each of these. The compositions (by weight%) were 80HfC/20SiC, 60HfC/40SiC, 40HfC/60SiC, 80HfC/20B_4C, 60HfC/40B_4C, and 40HfC/60B_4C. These powder bed samples were subjected to a 24 hour CVI run, following which they were mounted, sectioned and polished for microstructural observation. This analysis determined that the growth of the SiC matrix occurred primarily as a coating in the surface of the powder bed and that little infiltration of the SiC took place into the powder bed.

Table III. Oxidation results of particle bed study

Particle Bed Composition	Pre-oxidation Mass (g)	Post-oxidation Mass (g)	Mass Gain (g)	% Mass Gain
HfC-B_4C	0.743	0.696	-	-
SiC-B_4C	0.713	0.705	-	-
HfC-SiC	0.623	0.688	0.065	10.4%
B_4C	0.641	0.666	0.025	3.9%
HfC	0.974	1.074	0.100	10%
SiC	0.318	0.350	0.032	10%

CCI has infiltrated a cylindrical triaxially braided fiber preform with an 80HfC/20B_4C particle composition. The powders were dispersed in ethanol with a dispersant (menhaden fish oil) and then vacuum infiltrated into the fiber preform over three 20 minute cycles. The preform was then subjected to a 30 hour CVI SiC matrix densification run and the composite density profile across the thickness of the preform was analyzed by SEM. As shown in figure 12, the outer portion of the preform thickness is quite dense and the matrix has been deposited on and around the particles, as well as the fibers. Unfortunately, however, the open porosity has been closed off and this has precluded densification in the middle and inner surface of the preform thickness. Figure 13 is a micrograph from the middle of the preform thickness, showing that although particles have been infiltrated by the vacuum infiltration process, no matrix densification has taken place during CVI. This may be due to particles blocking infiltration of the precursor gases.

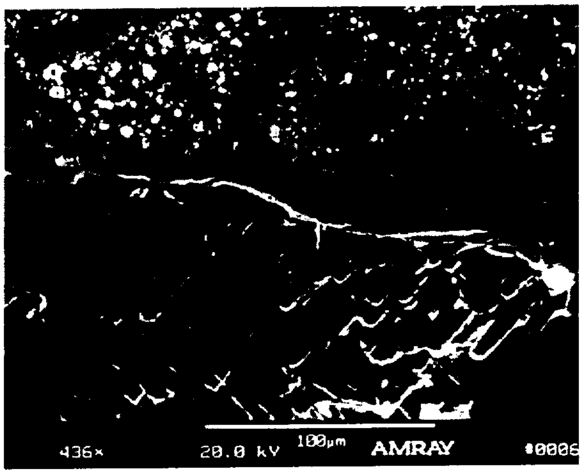

Figure 12. SEM micrograph showing the dense outer portion of the preform thickness (vacuum infiltrated with HfC-B4C then CVIed with SiC)

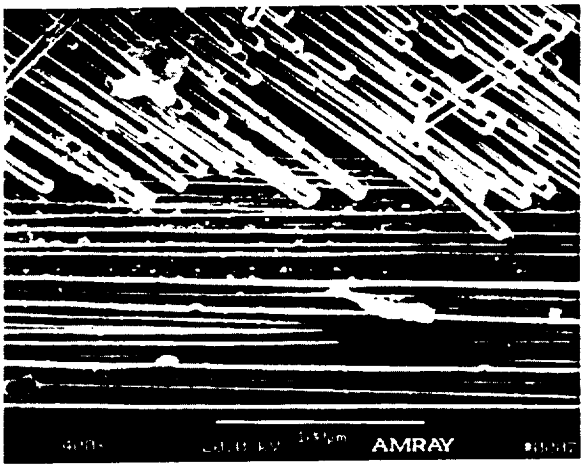

Figure 13. SEM micrograph showing the lack of matrix densification that has taken place in the middle of the preform thickness (vacuum infiltrated with HfC-B4C then CVIed with SiC)

Although the work carried out on this phase II research effort indicated that it was not possible to infiltrate gases into the powder packed fiber preform, more recent work on a DoE contract[6] has shown that by changing the CVI deposition conditions it is possible to promote densification within the fiber preforms. This has been achieved primarily by changing the gas pulsing cycle time to increase the time under vacuum (<50 Torr) and decrease the time at pressure (>50 Torr).

V. 4 Fabrication of test articles for NASA Glenn

A series of 6 pucks and a single $25lb_f$ thruster were fabricated as phase II deliverables for testing at NASA Glenn using H_2/O_2 propellants. The pucks were fabricated from material systems which had been down selected from the range of materials evaluated in this phase II research effort and which appeared best suited for the fabrication of propulsion components. The material systems which were selected were based on HfC/SiC and Re. A $25lb_f$ thruster was fabricated based on a Re inner surface functionally graded to C/C. Recent hot gas valve tests at Thiokol using solid propellants showed good behavior form this combination of materials and no erosion or degradation of the CMC following 5 seconds at 1500psi.

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[6] M.Patterson, "High Performance SiC-SiC Composites for Structural Fusion Reactor Components", DoE SBIR Phase I #DE-FG02-98ER82550, March 1999.

V. 4a Nozzle insert (Puck) fabrication

Six thick-sectioned composite tubes were fabricated using a two-step process in which a HfC/SiC composition was deposited throughout a 3D triaxially braided carbon fiber tube with an internal diameter of 1.0" and an external diameter of approximately 1.5". Following densification of the 3D braided preforms, these thin (0.25") walled tubes were inserted into a needle felted pitch based carbon fiber preform and densified by RTG CVI with a SiC matrix. The final densified pucks were then machined to the correct outside dimensions to achieve parallel faces between the two surfaces for effective clamping into the test rig. The final two pucks were produced from needle felted pitch based carbon fiber preforms functionally graded from a carbon matrix to a Re interior over the inner 30mils of the preform. Following Re deposition, the inner and outer surfaces of the pucks were machined to the dimensions shown in Figure 14. All six pucks have been delivered to Andy Eckel at NASA Glenn Research Center for testing in the gaseous O_2/H_2 flame rig. The composite rings will be tested at a O_2/H_2 ratio of 3 for 60 seconds and the diameter of the ring will be measured to determine the ablation rate due to oxidation. The O_2/H_2 ratio will be increased by 0.2 until significant erosion rates are measured.

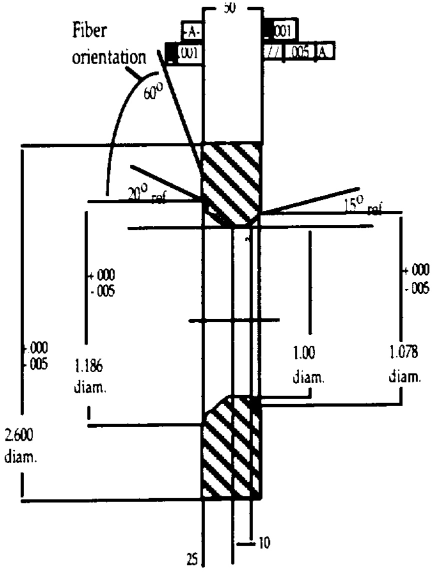

Figure 14. Dimensions of the composite pucks produced for testing at NASA Glenn

V. 4b Fabrication of the 25 lb_f thruster

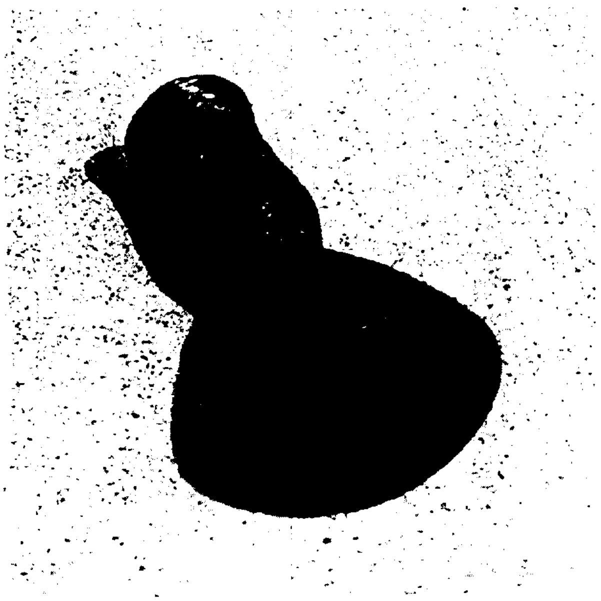

Figure 15. Photograph of the 25 lb_f thruster prior to testing at NASA Glenn

A graphite mandrel was machined to the dimensions of the standard NASA Glenn designed 25lb_f thruster and triaxially braided with M-30B carbon fiber to a thickness of 2.5mm. A pyrocarbon debond coating was applied to the preform for 6 hours and then the preform was removed from the mandrel and Re was deposited onto the inside surface of the thruster preform under isothermal conditions for approximately 30 hours. The Re coated thruster preform was then placed back onto the mandrel and carbon was deposited using RTG CVI. Following processing, a thin overcoat of SiC was applied to the outer surface of the thruster using isothermal processing for 8 hours. A picture of the as-processed thruster is shown in Figure 15. Machining of the attachment flange was performed before the thruster was shipped to NASA Glenn for testing.

VI. NEW TECHNOLOGY

During the period of this contract there were two potentially patentable discoveries which were made; one as a direct result of this work and the other as a result of additional work underway on composite development.

VI.1 Formation of HfC from solid C and Hf ($HfCl_2$ + methane).

As discussed previously, uniform infiltration of a HfC matrix via CVI is difficult and must be carried out slowely under carefully controlled processing conditions, ulually isothermal. For unknown reasons, infiltration of the precursor reactive gases ($HfCl_2$ + methane) that form HfC does not readily occur. CCI personnel have noticed that the $HfCl_2$ gas will react with solid phase carbon to form HfC under the CVI processing conditions. This finding was confirmed by a thermodynamic analysis using the HSC Chemistry for Windows program, which demonstrated that the formation of HfC from vapor phase $HfCl_2$ and solid phase carbon is favored, particularly if the amount of excess Cl_2 can be minimized. Experiments were conducted to determine the feasibility of improving HfC matrix infiltration/densification into a carbon fiber preform by infiltrating the $HfCl_2$ vapor and reacting it with a solid phase carbon source previously infiltrated/deposited as a discrete layer.

The initial experiments consisted of depositing alternating layers of carbon (methane reactive gas) and Hf ($HfCl_2$ reactive gas) to see if the $HfCl_2$ would in fact react with the previously infiltrated layer of solid phase carbon in order to form HfC. Hafnium metal was placed in a tube through which the chlorine gas entered the CVI chamber in order to form the $HfCl_2$ reactive gas. The introduction of the methane and $HfCl_2$ gases was alternated for 15 minutes each for a total run time of 6 hours. The results show that HfC was formed with excess layers of carbon. Excess C was observed in all the experimental conditions investigated, although it was clearly evident that the reactive gases ($HfCl_2$ + methane) reacted with the carbon previously deposited. If the processing conditions could be optimized for this process, this could be an alternative approach to carry out infiltration of HfC into the fiber preforms.

VI.2 Formation of Functionally Graded Re to $C_{(f)}$ /C Composites

During the same time period of this NASA SBIR Phase II research effort a parallel effort to fabricate Hot Gas Valves was underway in a Navy SBIR Phase I. The focus of this effort was to replace the expensive and heavy hot gas valves which are presently fabricated from solid Re or Mo alloys with a light weight substitute. For this purpose a functionally graded $C_{(f)}$ /C composite was fabricated and tested which was functionally graded to a dense Re interior over a 30 mil region. Careful processing of the Re and carbon matrices allow for the Re to be mechanically attached to the carbon fibers over a relatively large distance from the surface. This forms a very tenacious coating which performs well in hostile thermal environments and which can withstand erosion from solid propellants.

These functionally graded Re to $C_{(f)}$ /C composite valves were test fired at Thiokol using solid propellants. They were tested for 5 seconds at 450psi and a further 5 seconds at 1450psi and no erosion or weight loss was observed under these conditions.

VII. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The use of HfC matrices in carbon fiber CMC propulsion components is attractive since it offers the potential for long life operation at temperatures in excess of 4000°F (2200°C). The use of HfC alone in oxidizing conditions is subject to the formation of an unstable oxide which is continuously removed by "pesting," due to the tetragonal to monoclinic phase transformation in the HfO_2. Stabilization of the HfO_2 phase is therefore required and to this goal, this research initially investigated the deposition and testing of HfC-TaC CMCs. Early experiments showed that there were significant differences between the thermodynamics of formation of the Ta and Hf carbides, and that it was not possible to control the stoichiometry of the HfC/TaC solid solution deposited form chloride precursors. Experimental results showed that the yield for HfC at 1100°C and 1275°C is only 15% and 35%, respectively, resulting in fairly uniform deposits throughout the volume of the reaction vessel over all experimental conditions investigated. Although the CH_4 to Cl_2 ratio was suitable for HfC deposition, under similar conditions with $TaCl_x$ it was found that Ta or Ta_2C deposited in preference to TaC. The yield for TaC however appeared to be 100% over the complete temperature range investigated, namely 950° to 1275°C. The practical reality of this is that TaC deposits out form the $TaCl_x$ precursor onto the first how surface which is encountered, resulting in very non-uniform deposits throughout the volume of the reaction vessel. ***The stoichiometry of the HfC/TaC codeposit cannot therefore be spacially controlled.***

Attempts to laminate layers of TaC with HfC and anneal to form a HfC/TaC solid solution, while possible experimentally, the thickness of the TaC layer could not be controlled spacially. In addition, it was not possible to infiltrate the TaC into a fiber preform. The mixed HfC/TaC compositions which were fabricated and tested for oxidation resistance in an O_2-C_2H_2 flame did not show any conclusive trends which would support further reason to investigate the HfC/TaC system.

Other material systems and methods of producing them were investigated in the latter part of this research effort. Firstly, laminates of HfC/SiC were prepared in an attempt to anneal and form a solid solution which would oxidize to form a protective $HfSiO_4$ film to inhibit further oxidation. While moderately successful, it was identified that it was difficult to infiltrated HfC into the fiber preform and therefore this approach could not be used to control the HfC/SiC stoichiometry throughout the fiber preform.

A second approach to control stoichiometry between the HfC and second phase involved the infiltration of particles into the fiber preform to fill in the macroporosity. While vacuum infiltration of micron and submicron sized powders of HfC, SiC, B_4C, etc. into the fiber preform was possible, CVI of the filled fiber preforms resulted in early pore closure at the surface of the fiber preform. This approach shows considerable promise however, since the open porosity can be reduced form 70% to less than 50% and the infiltration of particles appears to be relatively uniform throughout the fiber preform - which would result in controllable stoichiometry.

Finally test components were fabricated for testing at NASA Glenn based on refractory, oxidation resistant surfaces functionally graded to a $C_{(f)}/C$ matrix.

A series of 6 pucks were fabricated based on materials which performed well during the phase II research. Four pucks were fabricated from equimolar HfC/SiC mixtures, 2 from laminates and 2 from co-deposits. Two additional pucks were fabricated functionally grading form a Re interior to a $C_{(f)}/C$ matrix. In addition to the 6 pucks, a 25lb_f thruster was fabricated based on a NASA Glenn design, with a Re interior functionally graded to a $C_{(f)}/C$ exterior. These components were delivered to NASA Glenn for testing with gaseous O_2/H_2 propellants.

In summary, this work identified the difficulties in producing mixed refractory compositions with HfC. The work indicated potential in pre-CVI processes such as particle infiltration into the fiber preform and in processes where the refractory surface deposit could be functionally graded to a $C_{(f)}/SiC$ or $C_{(f)}/C$ matrix.

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Ceramic Matrix composites based on HfC and TaC matrices have been fabricated by chemical vapor deposition and tested for use in long life, high temperature propulsion engine applications. The significantly different thermodynamics for these two material systems resulted in an inability to control the HfC-TaC stoichiometry.

Additional material systems were fabricated and tested and components based on HfC-SiC and on Re functionally graded to $C_{(f)}/C$ were selected for further testing.

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