Recapturing Graphite-Based Fuel Element Technology for Nuclear Thermal Propulsion

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ORNL is currently recapturing graphite based fuel forms for Nuclear Thermal Propulsion (NTP). This effort involves research and development on materials selection, extrusion, and coating processes to produce fuel elements representative of historical ROVER and NERVA fuel. Initially, lab scale specimens were fabricated using surrogate oxides to develop processing parameters that could be applied to full length NTP fuel elements. Progress toward understanding the effect of these processing parameters on surrogate fuel microstructure is presented.

I. Introduction

THE research presented in this report is a collaborative effort between Oak Ridge National Laboratory (ORNL) and NASA to recapture manufacturing technology for full length ROVER/NERVA graphite composite fuel elements. Nuclear thermal propulsion (NTP) fuel development has been intermittently ongoing since the late 1950's and many of the original materials used in the early fuel development are no longer available. Also, the processing capability and the art associated with the production of full-length elements have been lost. The focus of the collaboration is to recapture the capability and expertise to produce representative fuel element test samples and iteratively scale up to full-length elements. To maximize efficiency, the work was separated into two tasks, extrusion development and coating development, which were conducted in parallel. At this stage in the program, the extrusion development task is focused on recreating a representative blend of materials, evaluating blending methods, and establishing an extrusion capability. The coating task is focused on developing processing conditions and equipment to establish ZrC coating capability. This report summarizes the accomplishments and progression toward these goals. It is important to note that the results and analyses presented here are in the early stages of research (TRL 3) and should be considered preliminary.

II. Extrusion Development

The following section describes progress made on developing extrusion methods and characterization techniques for surrogate fuel element test samples.

A. Material Substitution

A specific goal for this program is to develop an extrusion blend that is most representative of the earlier work done for the NTP (Nuclear Thermal Propulsion) program, as well as identify blending methods for producing a uniform composite. The development process began with identifying materials used in earlier work. Some components are no longer available or the identification has change and there is no clear link to previous products. Substantial progress has been made in identifying the most suitable substitutes for these components. Table 1 outlines the typical materials and recipe historically used for fuel extrusion blend production.

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Table 1. Typical historical blend composition[1]

Component	Wt. % of component
Graphite	22.32
Carbon Black	3.94
Zirconium Carbide	51.62
Uranium Oxide (or surrogate)	7.46
Resin Binder	14.67

A typical fuel composite blend consists of five components; graphite, carbon black, zirconium carbide (ZrC), uranium oxide (UO_2) (or surrogate), and a resin binder. Several graphite materials have been used historically but the specific grades are no longer available or have been changed. In the latest work, synthetic graphite 5026 from Superior Graphite was identified as a suitable substitute for the original graphite material.[2] The carbon black used in the original work was manufactured by Thermatomic Carbon Company[3] but is no longer available. In later work, Thermax 135 from Cancarb was used[1] but has also been discontinued. For the current blend development studies, equivalent replacements were identified for the historical graphite and carbon black components. These materials closely represent the material used in previous work. The ZrC and HfO_2 (used in this work) are standard materials purchased from Sigma Aldrich. The most difficult component to replace has been the resin binder system. Thermosetting resin, Varcum 8251, consists of partially polymerized furfuryl alcohol and was used in the prior efforts but is no longer available.[1-3] Based on literature and knowledge of carbonizing resins, an attempt was made to recreate a “Varcum-like” resin.

B. Compact Fabrication

To begin developing composite blending and microstructure analysis techniques, a compacting method was utilized to produce “extrusion like” samples for evaluation until the extruder is installed and operational. The compacting method involves loading a die with the blended material and pressing it into a cylindrical geometry with a ram. The goal will be to use these samples to identify effective blending methods by looking at component distribution in a compact.

The compact fabrication method consists of blending the components (or replacements) identified in Table 1 in the appropriate weight percentages. Before mixing the components together, the resin was prepared by adding maleic acid to furfuryl alcohol in ratio of 4g/100cm^3.[3] The mixture was covered and left for one day at room temperature to catalyze. The dry powders were placed in a jar and mixed (shaken) thoroughly by hand. The resin mixture was added slowly to the dry powder and hand mixed with a spatula for 30 minutes. The mixture first created small spheres (~1/4” dia.) that finally broke up into smaller agglomerates. The consistency after blending was that of moist powder.

Two compacts were made using a hydraulic press and die set. NTP-comp-01 was made by pressing to 1000 lbf at room temperatures and holding for 2 minutes. This pressure was enough to squeeze the resin binder from the blend causing it to pool at the bottom of the die. NTP-comp-02 was made at 200 lbf. Pooling at the bottom of the die did not occur at this pressure. Figure 1 shows both compacts after being ejected from the die. An obvious density gradient that is characteristic of high L/D ratio compacts can be seen in the lower density compact (bottom).

Figure 1. Compacted NTP blend (green). NTP-comp-01 (top), NTP-comp-02 (bottom)

The two compacts were heat treated (low temperature) to 850°C under argon using the profile outlined in Table 3. This temperature is used to carbonized the resin binder and strengthen the sample. At this low temperature heat treatment, no physical change for the HfO_2 and ZrC particles is expected. At the end of last segment 3, the power was turned off and the furnace was allowed to cool uncontrolled to room temperature.

Table 2. Carbonization profile (bake out)

Segment	Temperature (°C)	Heating Rate (°C/min)	Duration (Hour)
1	20-250	0.1	38
2	250-850	1	10
3	850	hold	1
4	20	Furnace cool	NA

Figure 2 shows both compacts after heat treatment. The compacts held together well and were relatively strong. Some damage from handling can be seen on the ends. Table 4 provides a comparison of before and after carbonization measurements. It is important to note that the dimensions are approximations due to difficulty measuring.

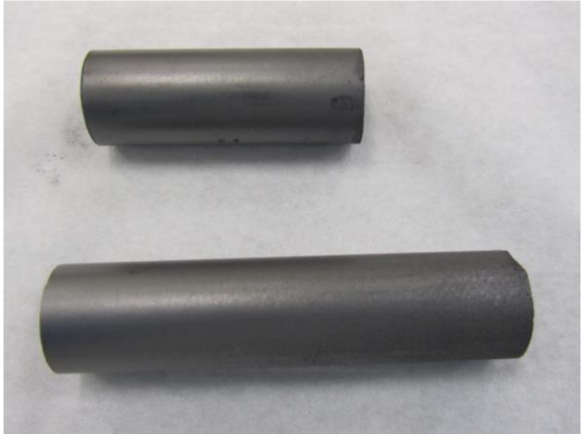

Figure 2. Compacted NTP blend carbonized. NTP-comp-01 (top), NTP-comp-02 (bottom)

Table 3: NTP compact dimensions

	NTP-comp-01			NTP-comp-02		
	Green	**Carbonized**	**% Change**	**Green**	**Carbonized**	**% Change**
Length (cm)	4.313	4.212	-2.3%	6.390	6.263	-2.0%
Diameter (cm)	1.531	1.522	-0.6%	1.531	1.508	-1.5%
Mass (g)	22.422	19.962	-11.0%	27.182	23.711	-12.8%
Density (g/cm^3)	2.82	2.60	-7.8%	2.31	2.12	-8.2%

C. Microstructure Analysis

After carbonization (850°C), a small (~1/4”) section was cut from the high density end of each compact. These sections were mounted and polished for optical evaluation. The following images show typical results from the analysis. Figure 3 shows that the HfO_2 and ZrC are distributed evenly throughout the compact. The large areas light grey colored areas are assumed to be resin that did not thoroughly blend. Additional blending techniques are being considered to eliminate this result.

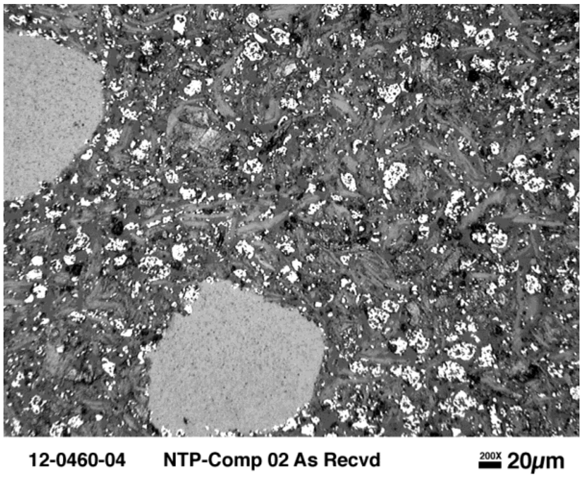

Figure 3: NTP-comp-02 (green)

In addition to optical analysis, an SEM was used to take images of the same cross section of the compacted samples. The backscattered SEM image (Figure 4) is used to confirm the presence and distribution of HfO_2 particles in a matrix of carbon and ZrC particles. Utilizing the SEM backscattering mode, the HfO_2 are shown as a slightly brighter white color than the ZrC particles which appear a light grey. The SEM used to take the images is equipped with an Energy Dispersive Spectroscopy (EDS) system. The EDS system was utilized to confirm the identity of each particle. Observing the shade difference between the HfO_2 and ZrC particles will become a significant aid for subsequent analysis.

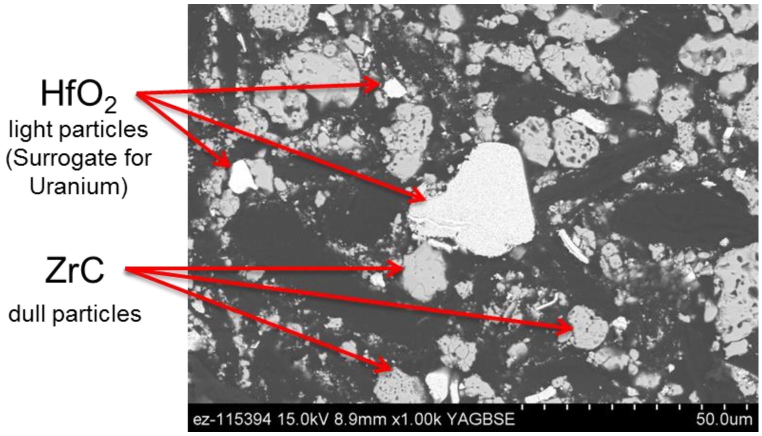

Figure 4: SEM image of compacted sample

The remaining compacted samples (not sectioned for optical analysis) were sent for an additional high temperature heat treatment. The high temperature heat treatment profile intended for the samples was a multi segment profile to 2700°C [3] providing adequate time and temperature for an interconnected network of diffused carbides to form. For actual fuel blends (containing uranium) the correct high temperature profile would create a coarse interconnected carbide network of solid solution (U,Zr)C. However, the blends used to make samples in this report have HfO_2 as a surrogate for UO_2 and are not expected to behave identically.

The actual temperature of the high temperature heat treatment is unknown due to technical difficulties with the furnace but estimated to be ~2400°C. During the furnace run, oxygen entered the furnace and allowed the outside edge of the sample to oxidize (remove graphite/carbon matrix). This revealed an interconnected network on the outer surface of the sample. This network may exist on the interior of the sample as well but further investigation is needed for confirmation.

Recall that after the low temperature heat treatment, discrete particles could be identified in the SEM images and that HfO_2 particle were brighter in color than the ZrC particles. This is no longer the case after the high temperature heat treatment of the samples as seen in Figure 5. During the high temperature heat treatment, particles diffused to form an interconnected network making it difficult to identify individual components. Although the particles cannot be discretely identified, bright areas can be seen throughout the network and provided evidence of Hafnium rich areas.

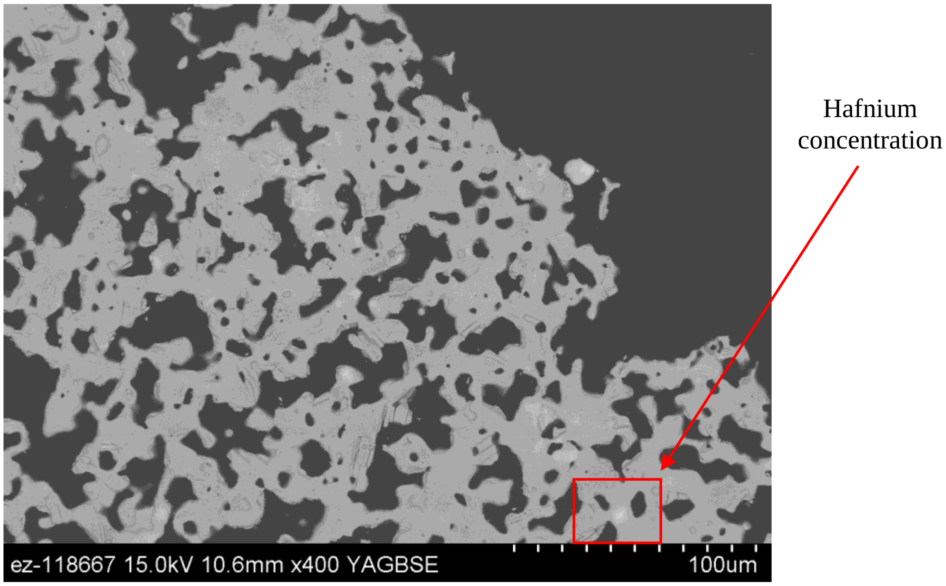

Figure 5. SEM image of interconnected carbide network for high temperature heat treated samples

Figure 6 is a magnified image of a hafnium rich area (center of top, left image) indicated in Figure 5. Grain boundaries can be seen between the once purely HfO_2 particle and the surrounding ZrC particles. The EDS system was used to create an elemental intensity map for carbon (red), Zirconium (blue), and Hafnium (green). Looking at the zirconium and hafnium maps, it is evident that the HfO_2 particle has diffused with ZrC particles to create the interconnected network.

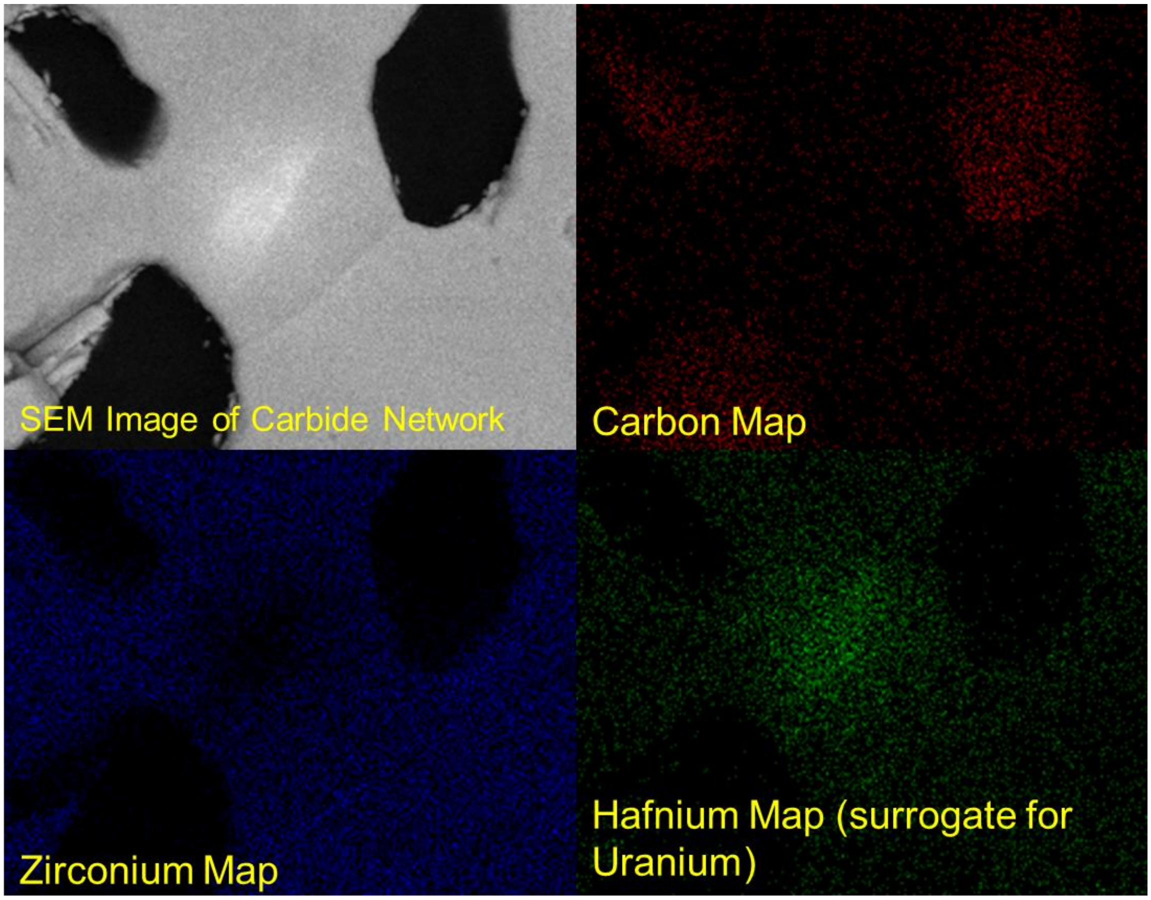

Figure 6. Element concentration map of interconnected network

D. Extrusion Development

A laboratory scale extruder (model 232-16 DT) was purchased from Loomis Products for the extrusion development work and is shown in Figure 7. The material cylinder for the extruder is 50 mm in diameter and 350 mm in length. Once the extruder was installed, an initial extrusion run was conducted to exercise the equipment and insure proper operation. For the initial fabrication development runs, a simplified die design (Figure 8) was used. The resulting extrusion from this die has a hexagonal cross section measuring nominally 0.75” across the flat and contains four 0.125” channels.

Figure 7. Extruder setup

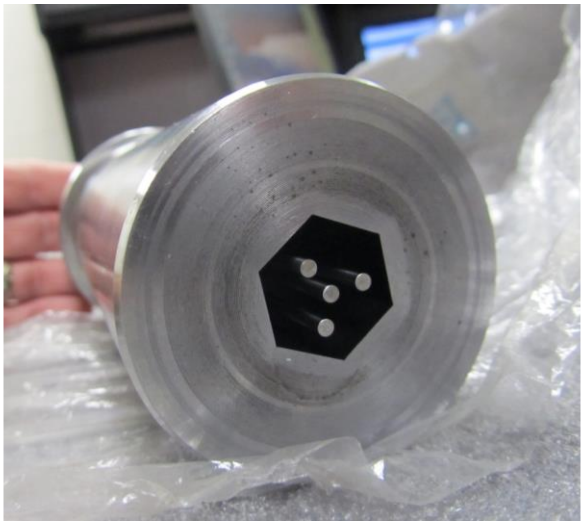

Figure 8. Hexagonal, 4-hole extrusion die set

For the test run, a 1000g batch of surrogate material was fabricated using the blend development techniques and recipe described in the compact fabrication section of this report. The only exception in the blend recipe was the substitution of ZrC with HfO_2 due to a limited quantity of ZrC. Once the batch was fabricated, it was loaded into the material cylinder. A vacuum was pulled on the material for approximately 30 minutes before extrusion began. Since the behavior of the extruder and extruded material was unknown, the extruder was operated by incrementally increasing pressure to keep the ram slowly moving.

The resulting extrusion is shown in Figure 9. The leading 2-3 inches of material was relatively low in density and was self-supporting. As the extrusion length increased, the density of the material increased and the extrusion became increasingly brittle. Only sections of 1-2 inches could be extruded before breaking from the die.

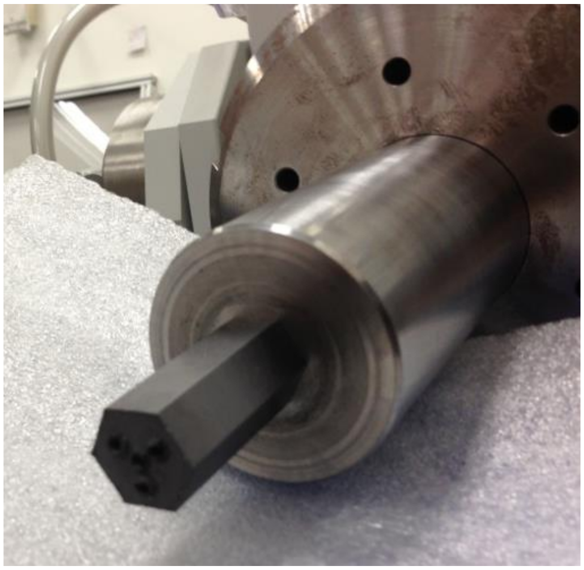

Figure 9. Extrusion results during initial test run

III. Coating Development

Zirconium carbide coatings on graphite substrates are being developed, at the Oak Ridge National Laboratory, in support of the NASA Nuclear Thermal Propulsion (NTP) project. These ZrC coatings will serve to protect the U-Zr-C composite fuel element from hot hydrogen erosion under operating conditions. This following section describes progress made on coating development.

E. Method:

A broad overview of the Chemical Vapor Deposition (CVD) process used for ZrC deposition during this project is as follows: Zirconium metal is chlorinated at elevated temperature to form zirconium tetrachloride ($ZrCl_4$) and mixed with Methane (CH_4) at sufficient temperature to facilitate thermal decomposition of the precursor gases and deposition of ZrC on the graphite substrate's surface. Argon is used as a carrier gas during chlorination of the Zr metal and excess hydrogen is passed through the system to form HCl from the free chlorine.

Existing Fluidized Bed Chemical Vapor Deposition (FBCVD) equipment was modified for operation under vacuum and to accommodate the coating of a single fixed specimen, rather than fluidized microspheres. For this work, the substrate consisted of a .75" diameter, commercially available, graphite rod with an axially centered through hole of historically representative size. Figure 10 shows a typical 6" substrate and typical method of cross sectioning. The substrate is cross sectioned in three places in order to observe coating microstructure as a function of axial position. During coating, the substrate resides in a conical graphite coating chamber surrounded by a resistively heated graphite element housed within a water cooled shell. Precursor gases follow a parallel path through the water cooled gas injector and Zr chlorinator until they intersect before entering the coating chamber.

Two separate methods were used to fixture the graphite substrates within the coating chamber. Initially the existing FBCVD coating chamber was used with the addition of a threaded fixture, located at the top of the coating chamber, which held the substrate in place (see Figure 11). Later coating runs utilized a revised one piece gas block and coating chamber which positioned the substrate directly over the gas inlet directing the coating gases through the internal channel and helping to ensure coating of this more critical area (see Figure 12). Also, with the revised design, the coating gases intersect within the gas block allowing them to mix before entering the substrate.

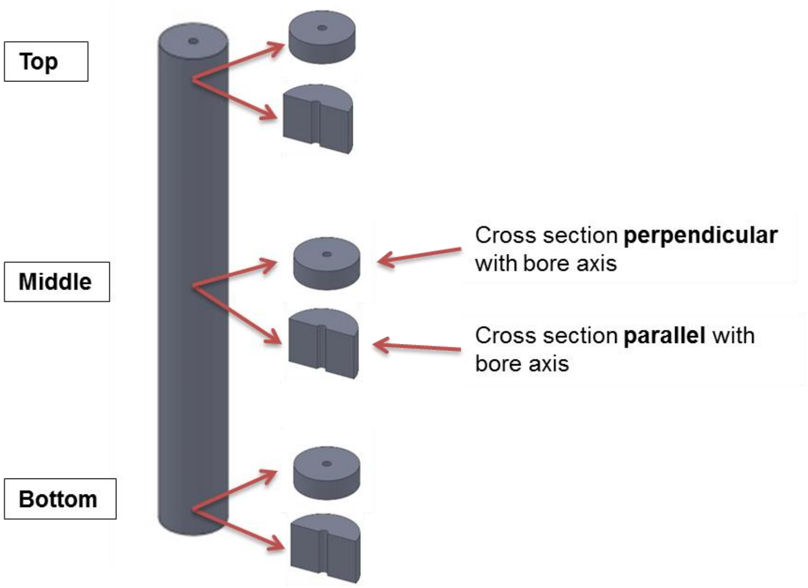

Figure 10. Typical 6" long graphite NTP specimen. Note: bottom corresponds to orientation within furnace, and that gas flow was from bottom to top.

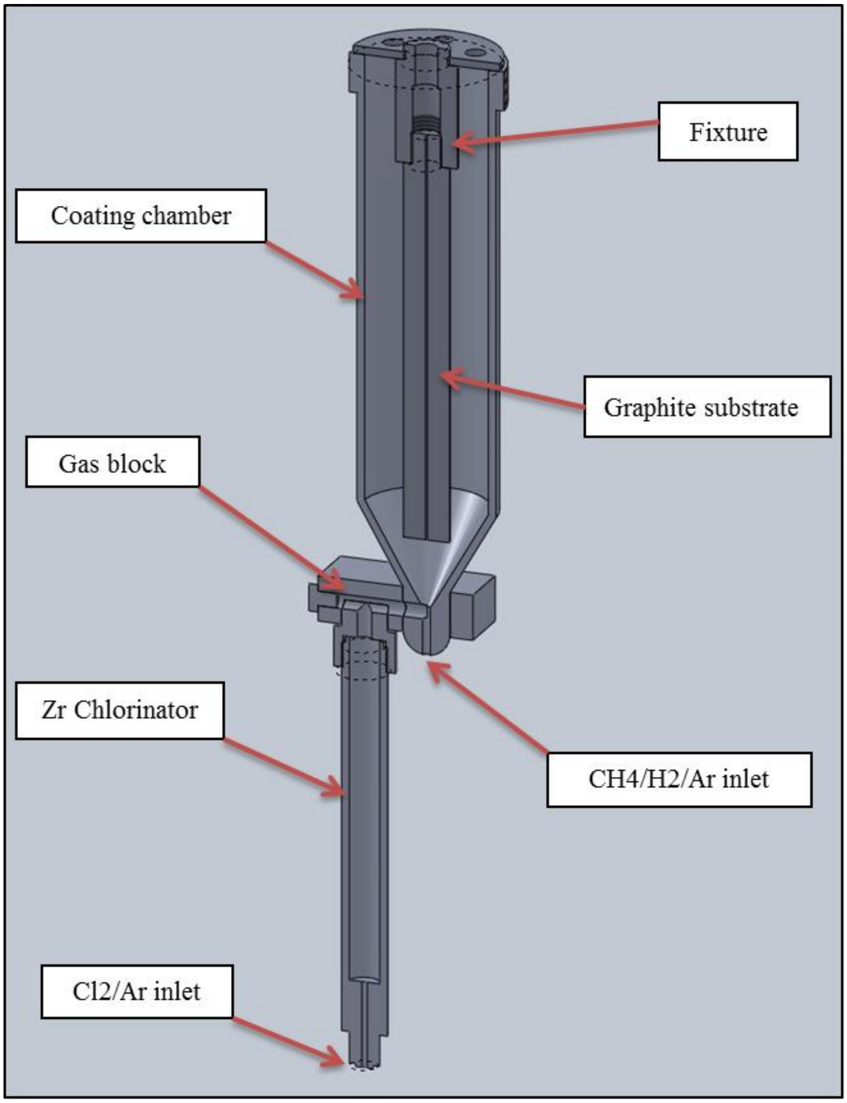

Figure 11. Modified FBCVD coating chamber, chlorinator and graphite specimen assembly

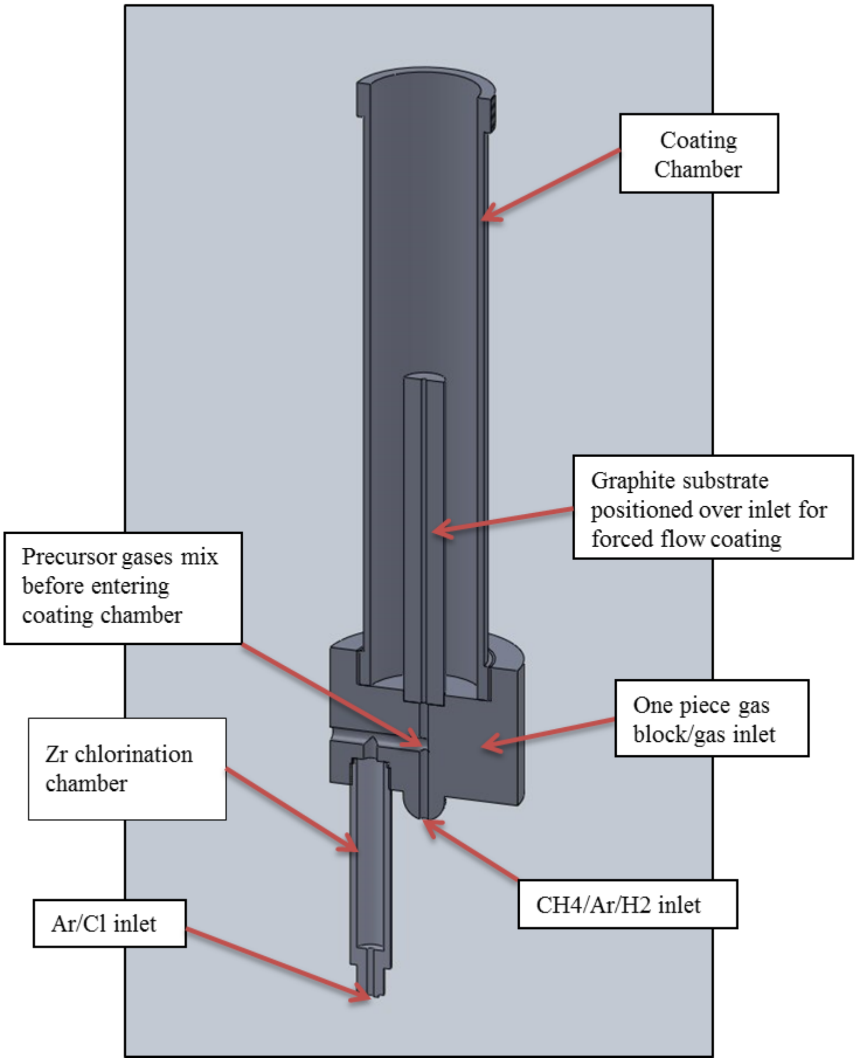

Figure 12. Forced flow coating chamber

F. Results and Discussion

Initial results, utilizing the modified FBCVD coating chamber, were encouraging in that ZrC was successfully deposited. However, as can be seen in Figure 13, ZrC deposition occurred primarily on the external surfaces with deposition only persisting a few hundred microns into the internal channel. This poor coating of the internal channel was due to precursor gas depletion and it quickly became apparent that a forced flow approach would be required.

Recent work has utilized the revised coating chamber design shown in Figure 12. Coating experiments have been performed under both reduced pressure and atmospheric pressure. NTPZrC-7 is an example of a reduced pressure forced-flow coating run. ZrC was successfully deposited on the internal channel, however the coating was not contiguous. A cross section of NTPZrC-7 (Figure 14) shows the irregular coating having a cauliflower type structure. This was likely caused by the ZrC growth rate being higher than the nucleation rate creating the islands of ZrC and uneven coverage.

The two most recent coating runs, NTPZrC-8/9, have utilized increased gas flow rates to move from a laminar to a turbulent flow regime. Turbulent flow is desirable from a precursor gas mixing and coating uniformity standpoint, but is generally not feasible for a variety of reasons.[4] However, ZrC deposition being a surface reaction and the small diameter bore geometry being used in this case allows for CVD coating in the turbulent flow regime and has proven successful. The Reynolds number (Re) within the internal channel for NTPZrC-8 was ~2100, approaching turbulent flow. Figure 15 shows the cross sectional micrographs of the bottom, middle, and top portions of the graphite substrate oriented both parallel and perpendicular to the bore axis. Coating thickness was ~30μm with good uniformity for the bottom and middle cross sections. Some cracking was evident from CTE mismatches between the ZrC and graphite substrate. The cross section from the top portion of the substrate however revealed an interesting dendritic microstructure. This coating variance was likely the result of gas composition change from depletion of reactant gases. Flow rates were further increased for NTPZrC-9 in turn increasing the Re to ~3000. Characterization results are pending.

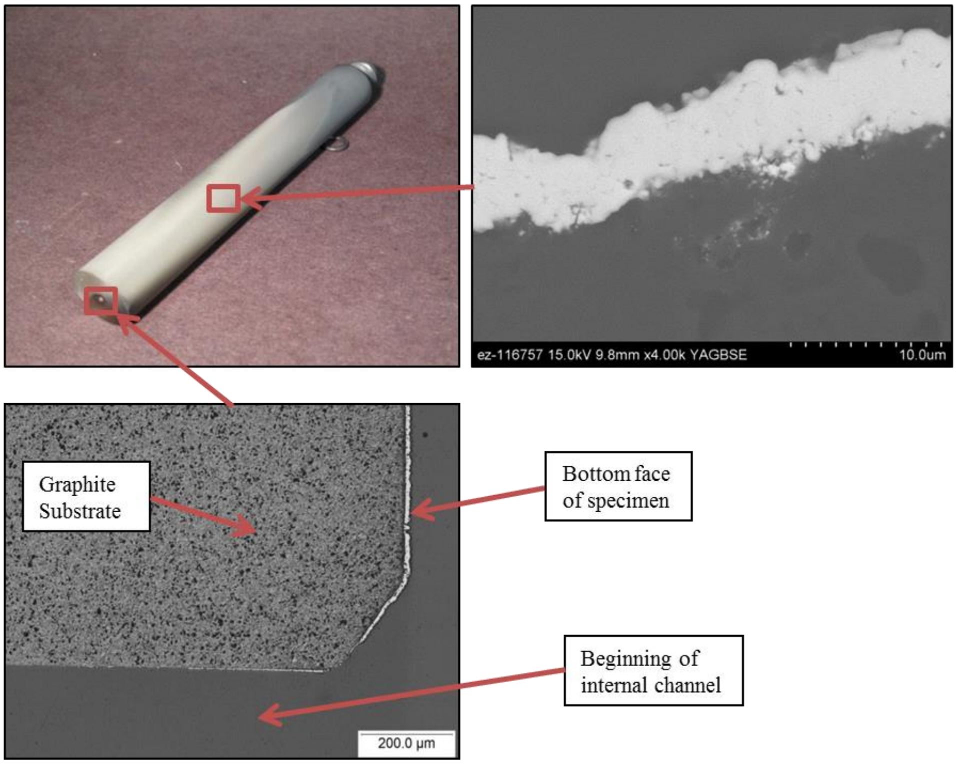

Figure 13. Cross section of NTPZrC-5 showing primarily external ZrC coating

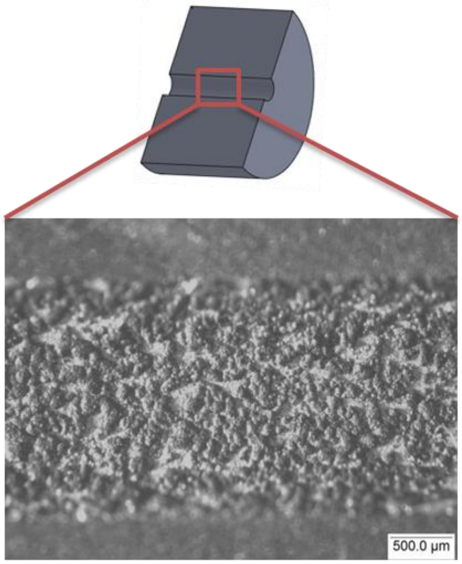

Figure 14. Cross sectional image of NTPZrC-7 (3X magnification)

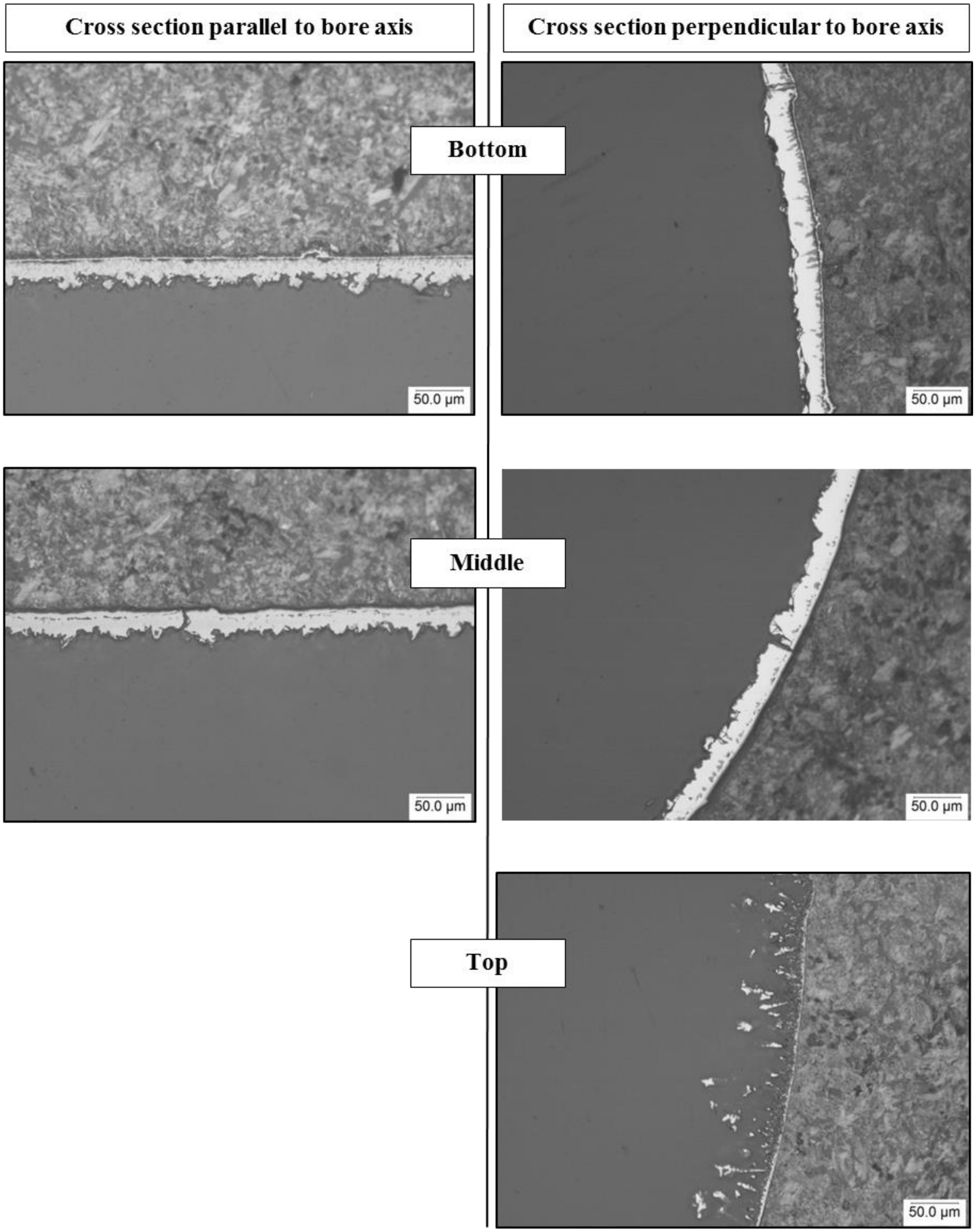

Figure 15. Bottom, middle, and top cross sections of NTPZrC-7 showing microstructural changes as a function of position (200X magnification)

IV. Conclusion

A collaborative effort was initiated to recapture the historical methods used to produce a ROVER/NERVA style fuel element. The fundamental research presented here for the NTP program at ORNL is essential in re-establishing the extrusion and coating capability required to fabricate full length fuel elements.

Under the extrusion development task, materials used historically for fuel fabrication were identified. Similar materials were identified as substitutes for materials that are no longer available. A compacting process was used to make samples for microstructure analysis. The analysis showed promising result including evidence of an interconnected network of HfO_2 and ZrC particle after the high temperature heat treatment. The extrusion capability has been established and utilized to produce initial test samples. Additional work is planned to optimize the material and extrusion process to fabricate longer and more representative fuel elements.

Coating development has progressed well. Initial experiments utilizing the modified FBCVD coating chamber were successful in depositing ZrC onto the surrogate graphite substrates, however the deposition occurred primarily on the external surfaces with little deposition within the internal channel. A revised coating chamber was designed and implemented which directed coating gases through the internal channel. Using this revised chamber, ~30µm ZrC coatings have been successfully applied within the internal channel. Future work will focus on optimizing processing conditions, which can be used to apply internal coatings on longer (16") specimens once new coating equipment is operational.

Acknowledgments

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