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Annual Summary Report: CY2024
Principle Investigator: Harrison D. Root, 505-537-2448, hdroot@sandia.gov; Sandia National Laboratories

Section I: Project Summary

Abstract: This report describes the proposed efforts for a three-year (CY23-25) program to develop refractory metal boride/carbide precursors for metal-organic chemical vapor deposition (MOCVD) applications. Reported are the CY24 results on the thermal processing of bis-cyclopentadienyl-dialkyl and tetra-alkyl precursors to obtain metal carbide products. Precursors evaluated are commercially available. Materials were processed within in a custom-built MOCVD system at 1000 °C, as well as in a hot isostatic press (HIP) at temperatures of 1000 °C or 1650 °C at pressures of 5000 psi. The products were identified as metal carbide, metal oxide, or a mixture of carbide and oxide phases depending on the starting material and process used. Density functional theory calculations were performed to determine the decomposition mechanism and to inform how ligand choice led to the products.

1. Overview of Project

Sandia National Laboratories is developing precursors to produce metal organic chemical vapor deposited (MOCVD) high temperature coatings (i.e., metal borides and carbides (Zr, Hf, and others)). These ceramic materials are of interest due to their ability to withstand ultra-high temperatures and wear conditions, which has led to its use in micro electro-mechanical systems (MEMS), magnetic storage, and other high temperature applications.[1-4] However, there is a limited number of commercially available precursors that have been successfully used under MOCVD processing conditions to generate the necessary stoichiometric metal borides/carbides. Sandia's synthesis, characterization and mod-sim capabilities are developing chemical starting materials that will lead to usable molecular MOCVD precursors.

The goal of this program is to develop tailored precursors that can be used for MOCVD processes to produce intercalated thermal protective coatings of metal borides (MB_x), and metal carbides (MC_y). The approach is to: (1) use molecular modeling to identify potential candidate precursors, (2) synthesize existing and new precursors, and (3) evaluate all precursors by MOCVD to produce MB_x and MC_y films and coatings. The objectives for this three-year program include: *Year 1*: Synthesize/obtain precursors with initial evaluation; *Year 2*: Verify Precursor Utility Under CVD Conditions; and *Year 3*: Optimization of volatility, purity, and quality of final films. Results are anticipated to overcome the limitations of commercial/state-of-the-art precursors used in vapor processing.

Previously, we proposed to generate metal borohydride group IV metal derivatives to act as MOCVD precursors for thermal protection systems (TPS) applications.[5-7] Results of this effort included understanding the stability of hafnium diboride precursors by identifying a potential decomposition intermediate ($Hf(BH4)_3H+BH_3$) and possible synthetic derivatives through density functional theory (DFT) atomistic modeling. In addition, deposition onto glass, steel and fibers (carbon, silica) were demonstrated through sublimation with hafnium borohydride [$Hf(H_3BH)_4$]

and bis-cyclopentadienyl hafnium borohydride $[(Cp)_2Hf(H_3BH)_2]$. While these are effective coatings, the precursors are difficult to synthesize, are unstable for long-term storage, and readily decompose. There observations are supported by the DFT atomistic studies. The instability of BH_4 species slowed and limited the development of useful precursors. Therefore, alternative precursors should provide more flexibility with longer shelf time, wider utility range, and higher quality films based to optimize processing. Shifting from BH_4 allows for a variety of potential ligands. For this approach, we will focus on developing ligand sets that bind directly between M-C (carbides) that would lead to greater retention and stability instead of using a bridging moiety to the necessary elements to form MC_x or MB_x.

This program directly impacts the Materials for Thermal & Chemical Extremes Program and the Hypersonics Aerodynamics, Heat Transfer and Materials Program by offering a means to generate protective, conformal coatings, with little to no expense on weight or size. By using molecular modeling, chemistry, and materials, we will undertake a fundamental study of known thermally protective species to develop new materials

Due to the limited library of reported MOCVD precursors for metal boride and metal carbide (MB_x and MC_y) materials, a systematic approach to generating these precursors was undertaken. DFT calculations were used to determine the appropriate decomposition pathways and to direct the synthesis efforts were carried out. Particular precursors were synthesized for MOCVD deposition of thermally protecting MC (M = Zr, Hf) films. The synthesis of additional precursors was performed this CY using standard glovebox, Schlenk line, and other air-sensitive manipulations. Once produced, each of the precursors will be fully evaluated by a variety of analytical methods (FTIR, multinuclear NMR (^{11}B, ^{1}H, ^{13}C), X-ray diffraction) to ensure the precursor has been made. Precursor volatility was tested by vacuum sublimation prior to testing in the MOCVD chamber to ensure useful films can be made.

Metal alkyls are ideal precursors to produce MC_x materials.[8-10] The direct M-C bond ensures a close interaction upon decomposition. While the benefits are numerous, the instability of the precursors offers challenges to produce stable precursors for MOCVD applications. Several methods are available to overcome these issues including steric and electronically bulking up the ligands. Numerous efforts using the cyclopentadienyl (Cp) derivatives have been reported, often with the 'problematic' issue of 'C' retention.[11,12] We can exploit this issue to favor carbide production. Further, allyls and mesityl derivatives have not been explored for MOCVD efforts. This leaves a wide path of precursors that can be developed for MOCVD applications, which when coupled with molecular modeling will allow for rapid down select of the appropriate approach.

An integrated approach using (*i) synthesis*, *(ii) modeling*, and verification of utility by *(iii) MOCVD film production* is being explored. As has been demonstrated, the synthesis and modeling studies work well to ensure a rational approach to precursor choice. All samples will be processed into coatings using MOCVD and the final materials characterized by analytical tools. These studies and results will generate a novel set of precursors for $M\text{-}C_x$ production, and eventually $M\text{-}B_x$, *via* MOCVD methodologies for TPS applications. Specifics for each effort are discussed below.

(i) Synthesis. Custom synthesized precursors will be synthesized and evaluated, with initial efforts focusing on materials which can be processed into carbide ceramics. The approach is outlined below, building on reported synthesis, molecular modeling, and applicability for MOCVD.

Several Hf/Zr-alkyl precursors have been reported.[13-14] Of interest are cyclopentadienyl derivatives (Cp) and tetra-alkyl derivatives as they possess a direct M–C bond, which we hypothesize will result in the retention of carbon in the resulting ceramic. Development of these compounds could be a facile route to the carbides. The resulting organometallic species are monomeric and tend to be volatile. Finally, while monomeric tetrabenzyl hafnium(IV) has been reported,[15] the mesityl derivatives have not been developed. Complex alkyls that cannot easily α or β eliminate H, or readily form unsaturated species (i.e., t-butyl groups forming butene), can frustrate organic leaving groups. As these systems are being developed, it is expected that the decomposition-products will retain C from the various organic moieties' decomposition forming MC_x and possibly MC_xH_y species. Refinement of the ligand and the alkyl groups (as directed by molecular modeling) will greatly direct the type of ligands to optimize synthesis of the desired ceramic phase.

(ii) Molecular Modeling. Modeling efforts will establish key precursor properties to tailor the volatility and decomposition temperature of the proposed compounds using density functional theory (DFT) electronic structure calculations in the *Fritz Haber Institute Ab Initio Molecular Simulation* (FHI-AIMS) and *Guassian16* codes.[16] With the shift in target molecules to those that contain Hf/Zr-L (L = B, C, Si) bonds, the stability of this bond and the impact of steric limitations on bonding will be evaluated. Bond strength[17] and chemical structure[18] has been shown to be an initial indicator of thermal stability since the 1960s and will provide a fast-initial screening for the large suite of proposed molecular structures. Here, the focus will be on evaluation of significant number of theoretical and candidate precursors, to provide direction for synthesis efforts. Candidate molecules will be down selected based on bond strength/structure and undergo more rigorous modeling to further refine a set of molecules for use as MOCVD precursors. Final results will include decomposition pathways and activation energies for the breakdown of the ideal MOCVD precursor, identifying controlling factors for molecular reactions under high temperature and the resulting formed products. Similar methodologies have been employed for the simulation of decomposition pathways in ammonium dinitramide,[19] copper and silver oxalates,[20] and tri-nitroethyl compounds,[21] among others.[22] This analysis will provide mechanistic information that can guide future metal/boron MOCVD precursor selection.

(iii) Production. Developed precursors will be evaluated for utility for MOCVD application. Our home-built MOCVD reactor system is comprised of a tube furnace wherein one side of the tube is fitted to a vacuum pump, allowing us to pull an active vacuum on the samples. The other side of our reaction tube is sealed so that no flowing gas, or atmosphere is used in processing. Samples can be placed in a crucible on the sealed end of the reactor, and substrates placed at varying distances along the tube length. The samples are heated to 1000 °C to induce volatility and decomposition. Material left in the crucible as well as deposited on the substrates can be evaluated as described below. The sealed side of the reactor can be connected to an external sample flask, allowing for varying the temperatures between sublimation and decomposition in the hot wall reactor. While this home-built system is being used for initial evaluation of the precursors, a commercial CVD system is currently being purchased to allow for fine tuning over the processing steps.

(iv) Film characterization. Once prepared from chemical vapor deposition processing, each sample will be evaluated for a continuous and complete ceramic coating that can survive the necessary temperatures. This will be accomplished from a variety of analytical, spectroscopic and microscopic techniques, including Powder X-ray diffraction (PXRD); Multi-nuclear Nuclear Magnetic Resonance Spectroscopy (NMR), Scanning electron microscopy (SEM). X-ray Florescence Spectroscopy (XRF) and X-ray Photon Spectroscopy (XPS), Raman Spectroscopy.

2. Activities and Accomplishments

In CY24 our team focused on the thermal processing of commercial zirconium alkyl precursors as a route to ZrC phases. Precursors were processed *via* hot isostatic press (HIP) and metal-organic chemical vapor deposition (MOCVD) routes. Additionally, DFT modeling has been implemented to evaluate decomposition pathways for these materials and preliminary modeling is being performed to evaluate decomposition to a carbide phase, which is absent in the current literature.

Molecular Modeling:

Molecular modeling efforts focused on using density functional theory (DFT) to calculate gas phase decomposition pathways for zirconocene based molecules to form zirconium carbide. Pathways were modeled for both molecular dissociation and beta-hydride elimination. The ideal CVD precursor would have the lowest disassociation energy (E_D) or reaction energy. The calculated dissociation energies for ligand removal are shown in Figure 1 and the dehydrogenation reaction mechanisms are shown in Figure 2.

The results show that hydrogen elimination is preferred over ligand decomposition. However, the decomposition energies did reproduce previous observations that ligands that have greater electron delocalization (larger ligands) would have lower decomposition energies.[23] A similar trend was shown with hydrogen elimination, that the “bulkier” ligands typically had lower reaction step energies.

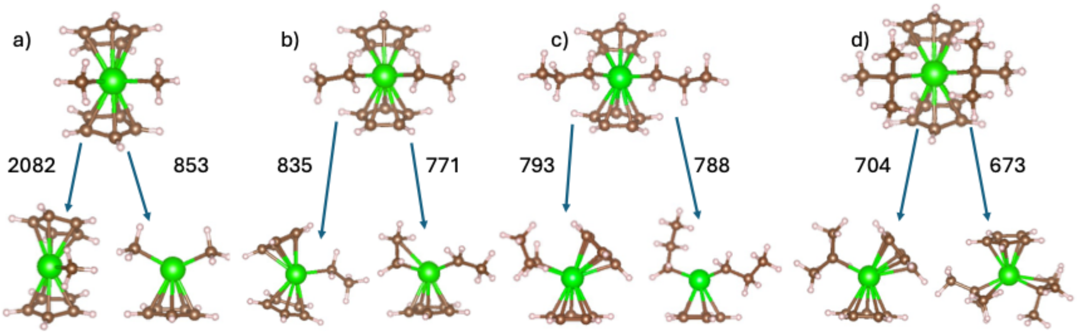

Figure 1. Calculated decomposition energies for four different zirconocenes with a) methyl, b) ethyl, c) propyl and d) iso-butyl ligands. Dissociation energies were calculated for alkyl and cyclopentadienyl ligand removal. Atom colors are green for zirconium, brown for carbon and white for hydrogen. Energies are in kJ/mol.

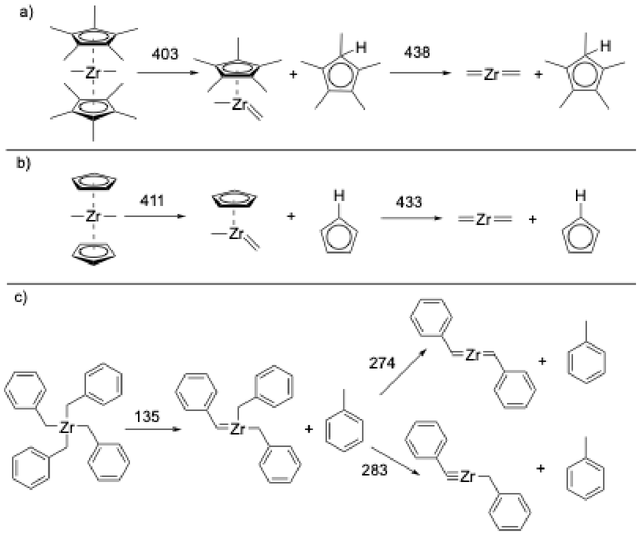

Figure 2. Beta-hydrogen elimination reactions for three zirconium precursors with reaction energies in kJ/mol.

The reaction mechanisms modeled eliminated the cyclopentadienyl (Cp) ligands from the zirconium centers, resulting in a dimehtylene-zirconium molecule for 2a and 2b, and a dimethylene phenyl zirconium in reaction 2c. Although the elimination of the Cp is endothermic, the dimethylene-zirconium stabilizes significantly in forming a molecular cluster (Figure 3), indicating that once formed, the molecules nucleate to form a quasi-ZrC structure.

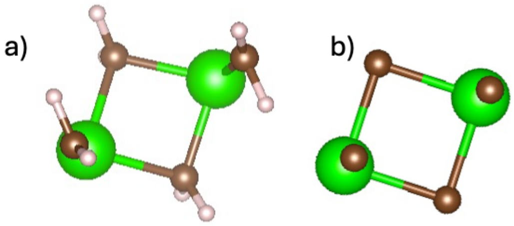

Figure 3. a) Optimized structure for two dimethylene-zirconium molecules compared to b) a section of zirconium carbide crystal. Atom colors are green for zirconium, brown for carbon and white for hydrogen.

Future efforts will expand upon completed work by adding temperature effects to get temperature representative Gibbs energies. Although reaction energies have been calculated for hydrogen removal, reaction barriers need to be calculated to help determine the total reaction energy barrier and the reaction step that could possibly be the rate limiting step. Additionally, further analysis needs to be completed for phenyl ligand precursors.

Synthesis and Processing:

Efforts this year focused on thermal processing of commercially available zirconium alkyl precursors as a route toward ZrC phases. The precursors evaluated were tetrabenzyl zirconium (**2**, Figure 4) and Bis(cyclopentadienyl)dimethylzirconium(IV) (**1**, Figure 4). These precursors were purchased from commercial suppliers and used as received. The purchased precursors were processed *via* an MOCVD type processing method where a crucible containing the ceramic precursor was placed on one end of a furnace which was then placed under vacuum. Substrates of silica were placed along the inside of the tube furnace and the furnace was heated to 1000 °C for 2 hours before being allowed to cool to ambient temperature. In addition to MOCVD, hot isostatic press (HIP) processing of these materials was also evaluated. In the HIP, the precursors were placed in a crucible and then subjected to 5000 PSI (argon) while being heated to either 1000 °C or 1650 °C, held at temperature for two hours, and then allowed to cool to ambient temperature. Post processing, the resultant materials were evaluated by SEM, PXRD, and EDS to determine the identity and phase of the product.

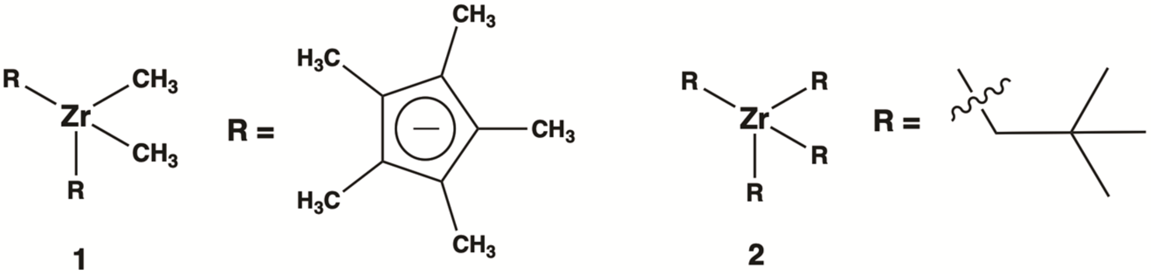

Figure 4. Commercial chemicals evaluated as ZrC precursors.

Hot Isostatic Press (HIP) Processing

The HIP is an instrument that is capable of heating materials under pressure to reduce the porosity of metals/ceramics and increase their density (Figure 5). Capable of achieving pressures up to 30,000 PSI and temperatures up to 2250 °C, we believe this processing method allows a comparable, parallel processing approach to the MOCVD thermal processing method. In a typical process, our ceramic precursor was placed in a crucible within the instrument and heated to either 1000 °C or 1650 °C under 5000 PSI (argon) and held at temperature for two hours. Upon cooling, the resultant product was removed from the crucible and tested to verify identity and phase.

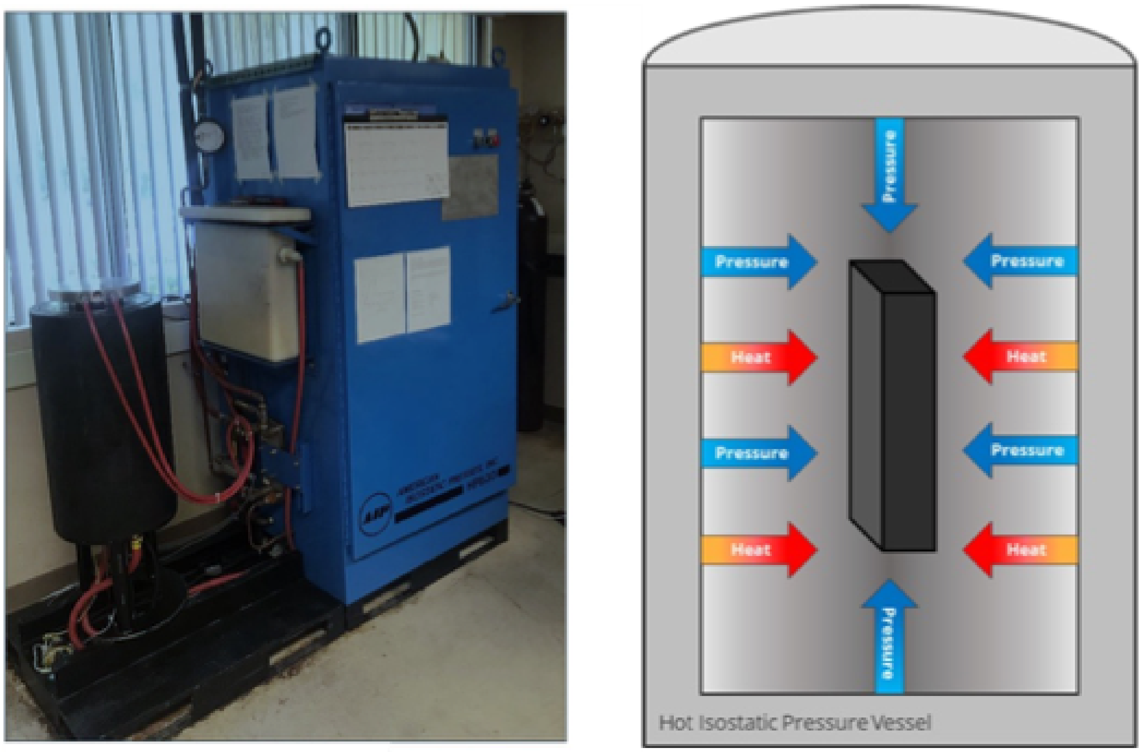

Figure 5. Hot isostatic press instrument.

HIP processing of both **1** and **2** at 1000 °C resulted in mixed phases of ZrC and ZrO_2 (Appendix A. Figure 12). Interestingly, the product resulting from **1** resulted in micron-sized spherical particles (Appendix A. Figure 13) and EDS did not indicate a large presence of oxygen, while additional peaks which could be attributed to ZrO_2 were observed in PXRD, although broad peaks and low intensity made deconvolution difficult (Appendix A. Figures 12). The product resulting from processing **2** *via* the same method did display peaks which were attributable to both ZrC and ZrO_2 in the PXRD (Appendix A. Figure 16), as well as an appreciable oxygen peak in XPS (Appendix A. Figure 17). Notably, the morphology of this product was more akin to plates/flakes (Appendix A. Figure 15).

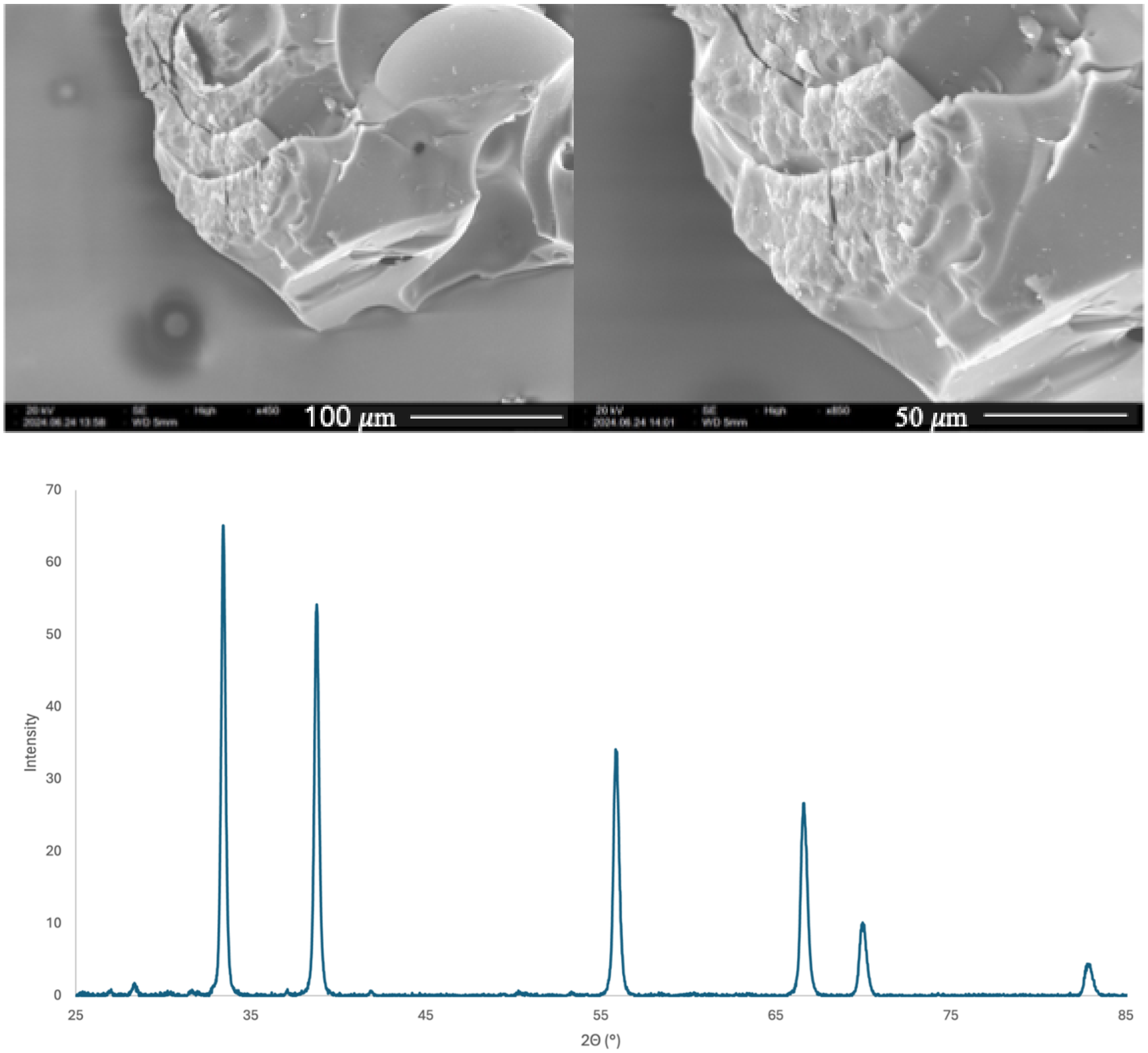

Figure 6. SEM and PXRD of product resulting from **1** in HIP process at 1650 °C, 5000 psi, 2hrs. PXRD shows highly crystalline ZrC material.

Increasing the processing temperature for both **1** and **2** in the HIP from 1000 °C to 1650 °C resulted in products with notably higher crystallinity, and easily identifiable as ZrC by PXRD, with no indication that oxide was phase was present (Figure 6, Appendix A. Figures 18 – 20). Additionally, the morphologies of both materials resembled flakes, rather than particles observed at lower temperatures (Appendix A. Figure 18).

Through our efforts in HIP processing of commercially available zirconium alkyl precursors, we have demonstrated the utility of these precursors in the production of MC_x ceramics. This family of precursors readily results in carbide ceramics with minimal (to no) oxygen present in the final material. Ongoing efforts will focus on custom synthesized precursors, where varying the alkyl substituent will allow for tailoring the processing temperature to optimize MC products yield.

Metal - Organic Chemical Vapor Deposition Processing (MOCVD)

In addition to HIP processing of the commercial zirconium precursors, a pseudo-MOCVD process was also explored in which precursors were evaluated for both the product of their thermal decomposition and their ability to be transported in the gas phase to deposit coatings. In this processing method, a home-built CVD system was used to heat the precursor materials in a hot-wall reactor under active vacuum with no flowing gas. The entire CVD system is contained in an inert environment glovebox to prevent oxidation of the precursors prior to processing. Substrates were placed at various positions along the furnace tube, to capture any deposition at varying distances from the precursor position (Figure 7).

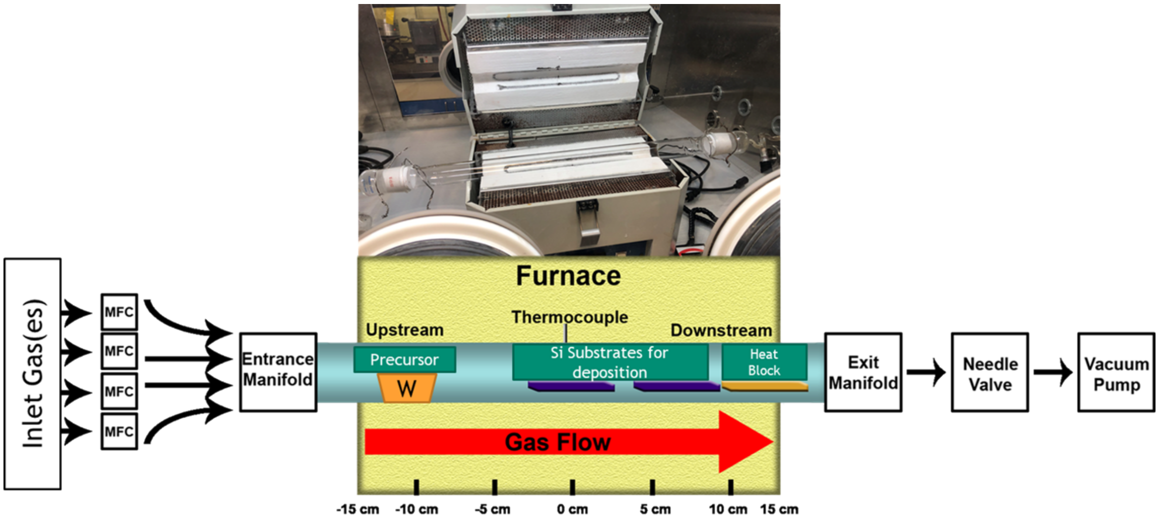

Figure 7. Photo of tube furnace reactor used for the processing of metal alkyl precursors in an inert gas or vacuum environment. Illustration below represents overall design of reactor with gas inlets and vacuum outlet ported through glovebox wall, and an example of precursor and substrate positioning. Exact positioning of precursors and substrates varied across replicate processing runs, and both alumina and tungsten crucibles were used.

Samples processed by this method were heated at ramp rates of 5 – 20 °C/min to 1000 °C and the temperature held for 2 hours before being allowed to cool to room temperature. Material which remained in the upstream crucible was analyzed by PXRD, SEM, and EDS, while films deposited on Si substrates were characterized by SEM and EDS.

Processing of **1** resulted in a uniform, dark grey deposit throughout the reactor, with minimal product remaining in the crucible. PXRD from the material remaining in an Al_2O_3 crucible resulting from the thermal processing of **1** indicated phases of both ZrC and ZrO_2 as shown in Figure 8, with the dominant phase being the oxide product. Oxygen contamination may have occurred from precursor decomposition during transfer into the reactor glovebox post synthesis or may have come from reaction with the alumina crucible. Given this, tungsten or carbon crucibles were used moving forward, which resulted in insignificant product remaining in the crucible post processing, suggesting that **1** is a potential candidate to further optimize conditions for vapor transport and deposition. Supporting this analysis, EDS showed characteristic peaks related to carbon, oxygen, and zirconium.

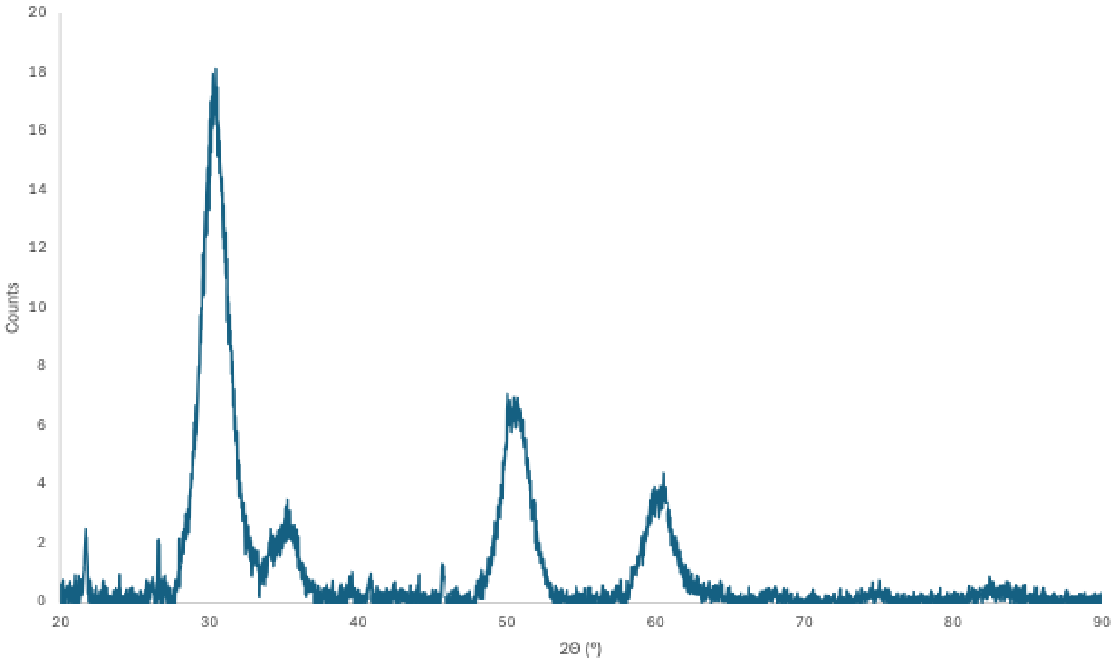

Figure 8. Powder X-ray diffraction pattern of the product of the low-pressure decomposition of precursor **1** in the MOCVD apparatus.

Interestingly, the products deposited on the downstream substrates showed different morphologies, depending on the substrate placement, with variety of observed products shown in Figure 9. The Si wafer substrate located upstream, adjacent to the precursor source shows a variety of products including micron-sized ceramic deposits and knobby clusters, which EDS indicates may be Zr doped carbon. The cluster product morphology was found across precursors evaluated and throughout the upstream and middle regions of the reactor. A unique product was observed consisting of flaky products which appeared to grow into thin ribbons of product, which EDS qualitatively indicates presence of both Zr and C. The samples were analyzed using XRD without removal from the Si wafer substrate, but no appreciable signal (distinguishable from baseline) was observed that would identify the deposited products. The large ceramic deposit was a minority product and may have been transferred from the decomposed precursor crucible either during processing or post processing as either a result of repressurizing the system or during product and substrate removal.

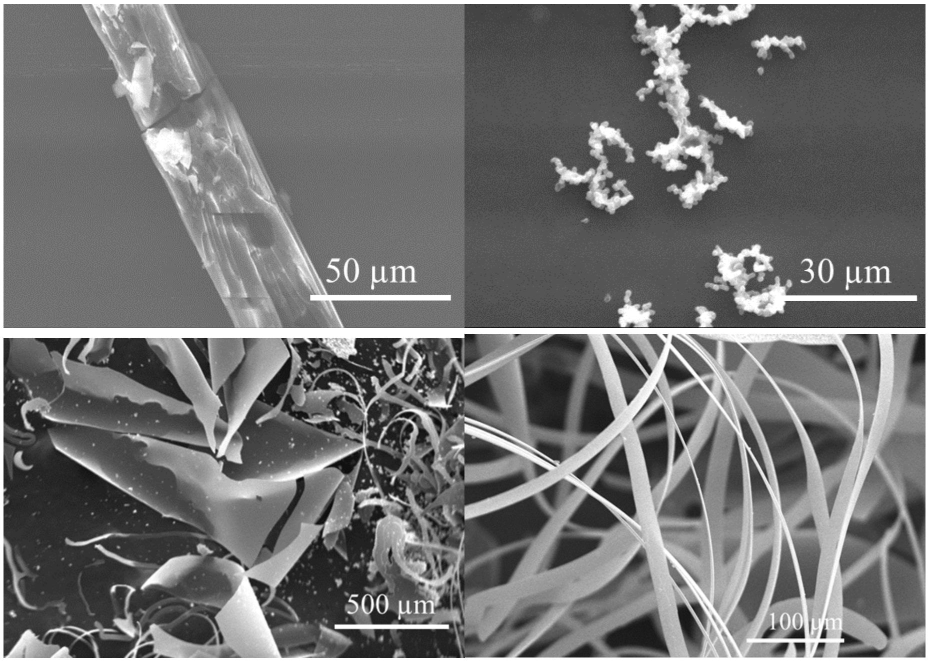

Figure 9. SEM images of the variety of products observed from the thermal decomposition and MOCVD processing of precursor **1**. The upper left image shows a large ZrC deposit on the Si substrate nearest the precursor crucible. The upper right image shows the predominantly carbon "clustered" product. The lower images show the flake and ribbon products observed at the furthest downstream substrate, located at the edge of the heating zone.

When precursor **2** was processed *via* our MOCVD system, we observed very little deposition of material on the downstream substrates, the majority of the processed material remained in the upstream crucible, with W crucibles used for all processing. This remaining solid was characterized to be primarily ZrC product. PXRD and EDS both support the conclusion that carbide was formed, with minimal side reactions to zirconium oxide, although the lack of volatility/deposition of the material brings into question the material's utility as a CVD precursor. PXRD from the material remaining in the crucible resulting from the thermal processing of **2** indicated the successful formation of ZrC as shown in Figure 10. Presence of additional phases or compositions, such as oxides from contamination or nitrides from the glovebox environment, is possible, but no refinement of the pattern was not conducted. The XRD pattern shown in Figure 10 has relatively low intensity of peaks and significant broadening, potentially coming from a lack of crystallinity or the wide variety of stable ZrC_x products where X=0.65-0.98.

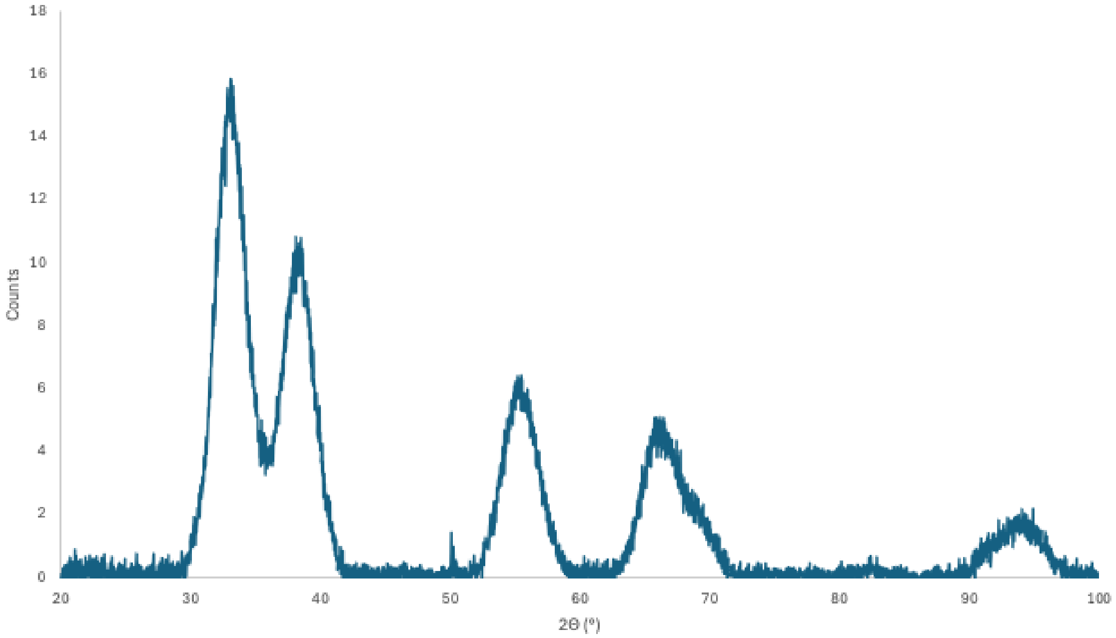

Figure 10. X-ray diffraction pattern showing the decomposition of **2** indicating the presence of ZrC.

In addition to the XRD, SEM and EDS analysis are consistent with this conclusion, showing a bulk crystalline product consisting predominantly of Zr and C, with some presence of O for the product remaining in the crucible. Deposition of a uniform, grey film was observed on the reactor walls and downstream substrates consistent with what was observed for reactions using **1**. The products observed on the downstream substrates were shown to be C, with a similar nodular cluster morphology as seen previously and shown in Figure 11 B and C.

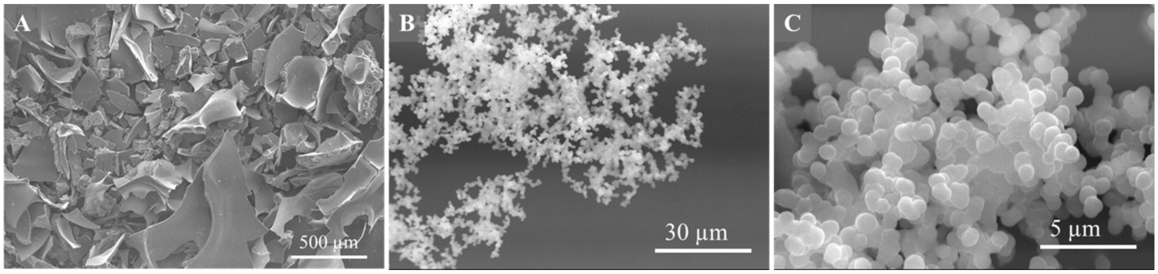

Figure 11. SEM images showing the ZrC and C products formed through the decomposition of precursor **2**.

3. Findings and Conclusions

This CY, commercial precursors were evaluated as MOCVD precursors towards ZrC ceramics. These commercial precursors were processed by MOCVD, as well as HIP to evaluate their volatility, as well as their propensity to convert to a carbide phase. It was determined that the evaluated Zr alkyl precursors could be effectively converted to the desired carbide ceramic, and are volatile enough to transfer to substrates downstream, although alkyl identity does have an impact on the volatility and material transfer. Moving forward into next year, we will continue the synthesis of custom precursors and evaluate the structure – property relationships of the precursors as they are converted to UHTC phases.

4. Plans and Upcoming Events

- Finalization of manuscript on Evaluation of the Stability and Structure of Candidate Zr/HfC precursors.
- Purchase commercial MOCVD instrument.
- Continue synthetic efforts of custom precursors.
- Propose mechanism for conversion to carbide from molecular precursor.

5. Transitions and Impacts

Precursors developed through this program will be compared to current state-of-the-art precursors employed by ONR for CVD processing by correlating binding energies and thermal properties. We will develop our transitions plan as candidates are determined.

6. Collaborations

We are working on developing and are in communication Babak Anasori (Purdue), Thomas Gray (Case Western), and Rebecca Sweat (FAMU) for collaboration opportunities.

7. Personnel

Principal investigator: Dr. Harrison D. Root (Sandia National Laboratories)
Co-investigator: Dr. Jacob D. Boissiere (Sandia National Laboratories)
Business Contact: Cheryl Perea & Kelly Rilley (Sandia National Laboratories)
Team Members: Dr. Matthew Christian (Sandia National Laboratories); Ms. Samaiyah Mason (Sandia National Laboratories, Florida A&M University); Ms. Zipporah Harlan (Sandia National Laboratories, Florida A&M University); Subs: None

8. Students:

Number of graduate summer students assisting during reporting period: 2

9. Technology Transfer

It is expected that patent applications will be pursued once new compounds have been identified. Precursors developed through this program will be compared to current state-of-the-art precursors employed by ONR for CVD processing.

Products, Publications, Patents, License Agreements, etc.

Publications resulting from this project:

One manuscript in preparation: Boissiere, J. D.; Christian, M. S.; Mason, S.; Harlan, Z.; Root, H. D. "Thermal Processing and Decomposition of Refractory Metal Cyclopentadienyl complexes" *Manuscript in preparation*

Archival Publications (publication reference information (article title, authors, journal, date, volume, issue) can be automatically entered using a DOI)

a. Article Title: Stability Evaluation of Candidate Precursors for Chemical Vapor Deposition of Hafnium Diboride (HfB_2)
b. Journal: ACS Omega
c. Authors: Jessica M. Rimsza, Samuel C.B. Chackerian, Timothy J. Boyle, Bernadette A. Hernandez-Sanchez
d. Keywords: density functional theory (DFT); $[Hf(BH_4)_4]$
e. Distribution Statement: N/A
f. Publication Status: Published (*CS Omega* 2021, 6, 17, 11404–11410)
g. Publication Identifier Type: https://doi.org/10.1021/acsomega.1c00391
h. Publication Identifier: The unique identifier for the publication
i. Publication Date: April 23, 2021
j. Volume: 6
k. Issue: 17
l. First Page Number: 11404
m. Publication Location: USA
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o. Peer Reviewed? Yes

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Appendix A: Supplementary data

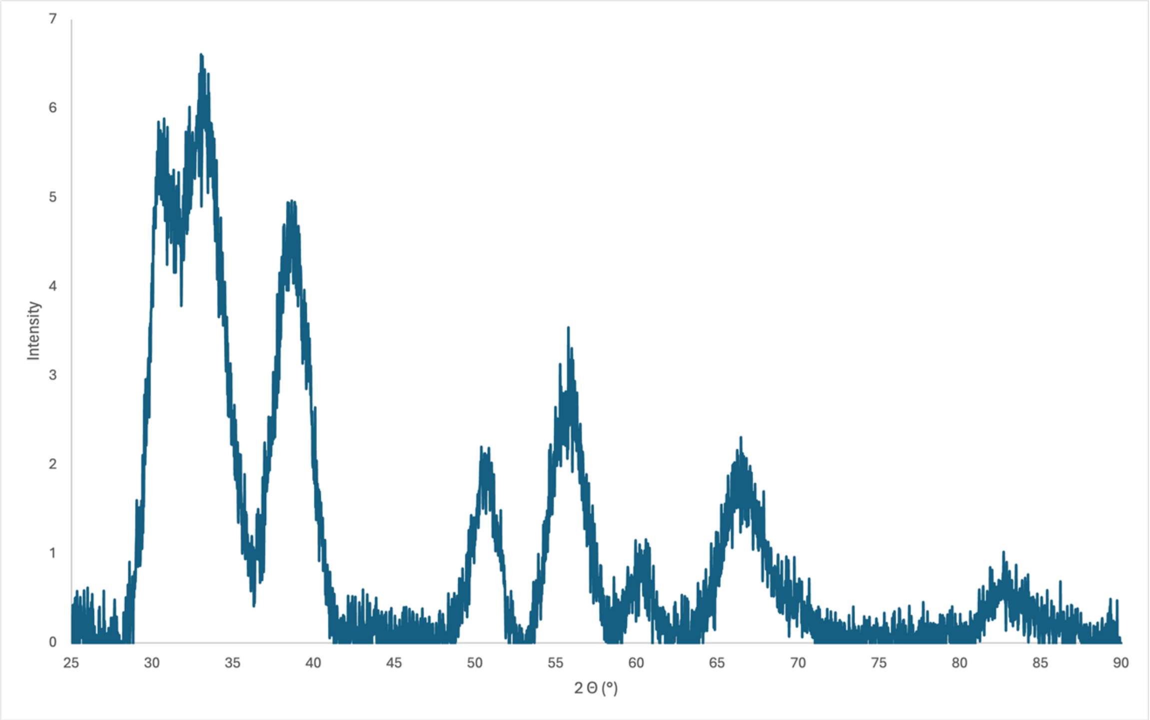

Figure 12. PXRD of product resulting from HIP processing **1** at 1000 °C, 5000 psi, 2hrs.

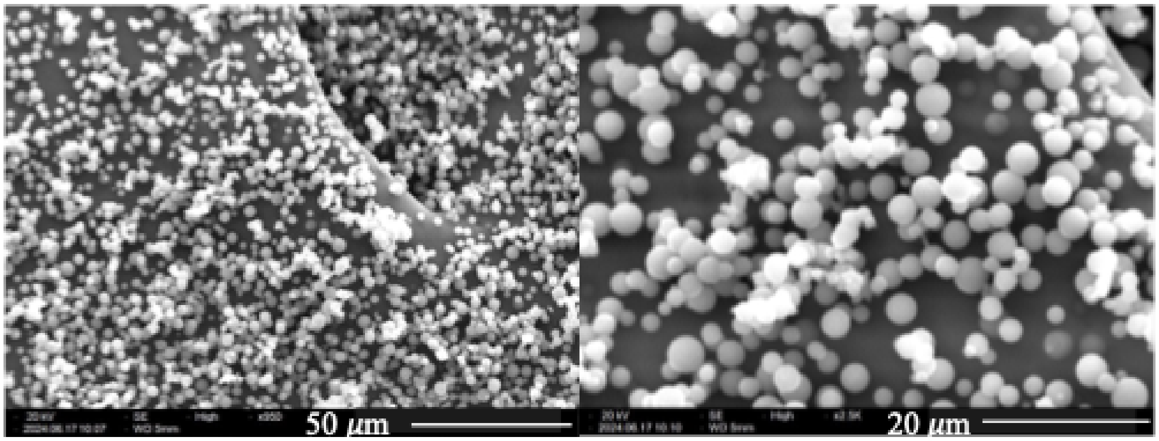

Figure 13. SEM images of product resulting from HIP processing **1** at 1000 °C, 5000 psi, 2hrs.

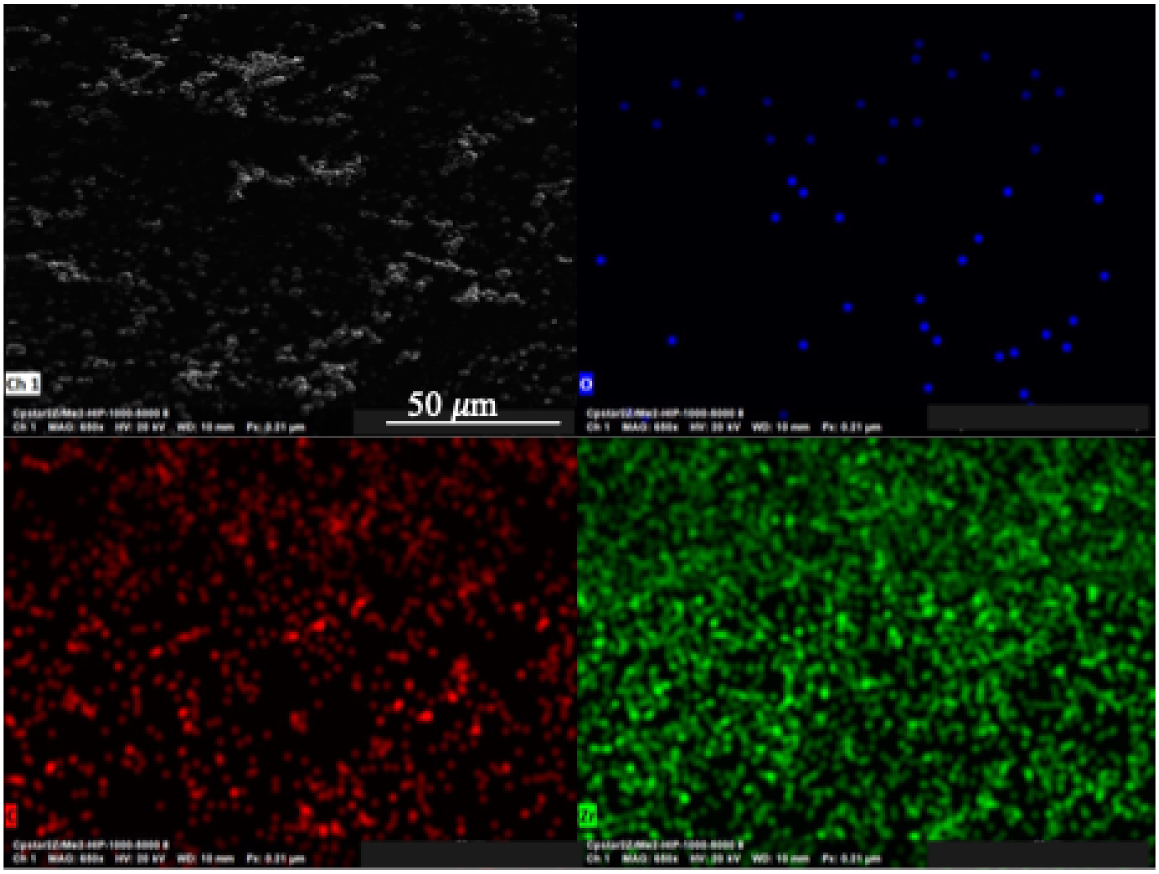

Figure 14. Elemental mapping of product resulting from HIP processing **1** at 1000 °C, 5000 psi, 2 hrs. Minimal oxygen is observed.

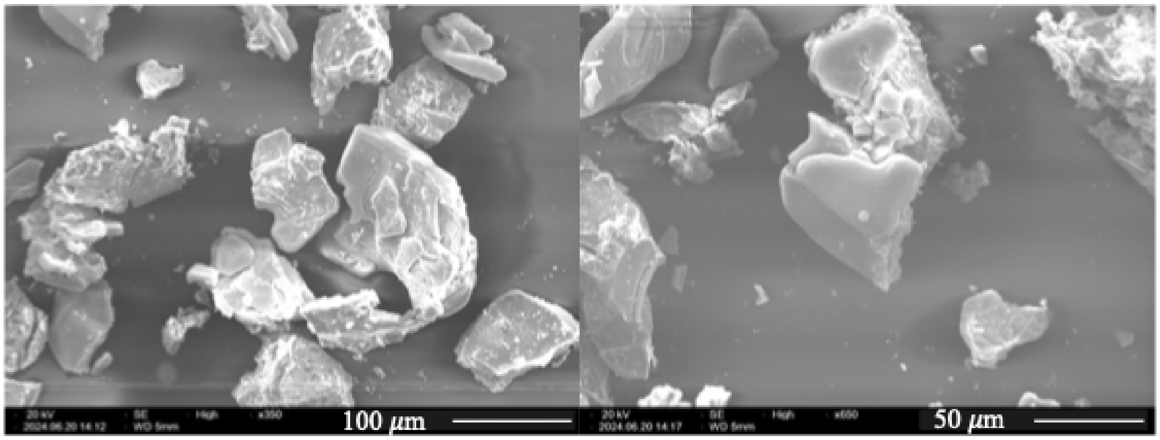

Figure 15. SEM of product resulting from HIP process of **2**, 1000 °C, 5000 psi, 2 hrs.

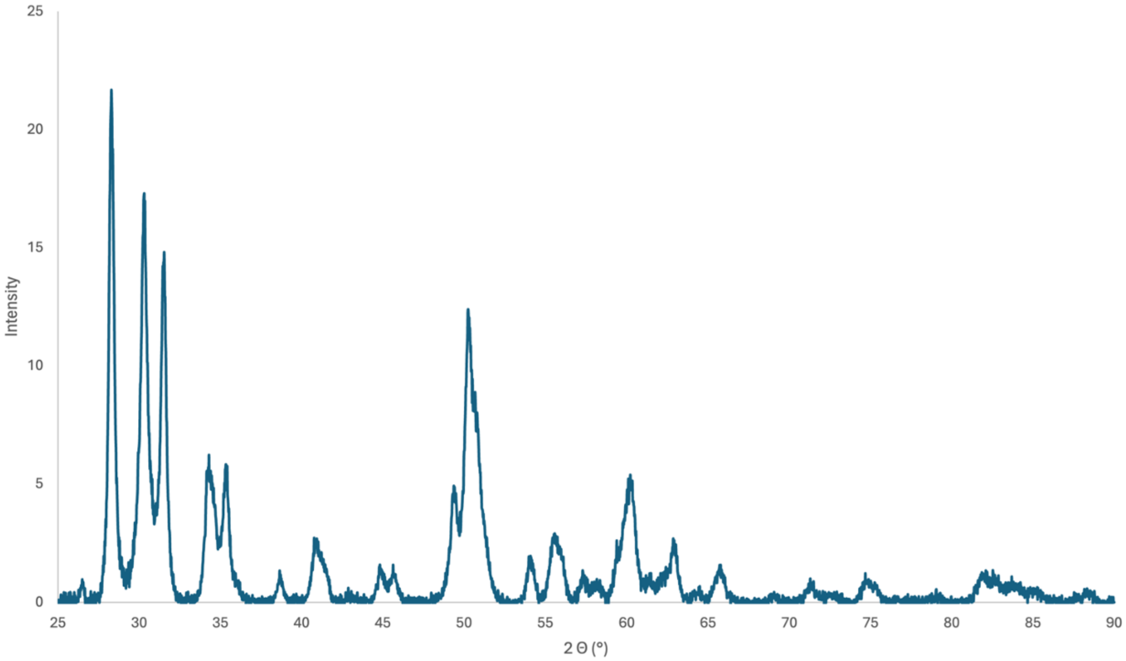

Figure 16. PXRD of product resulting from HIP process of **2**, 1000 °C, 5000 psi, 2 hrs. PXRD peaks indicate presence of both zirconium carbide and oxide phases.

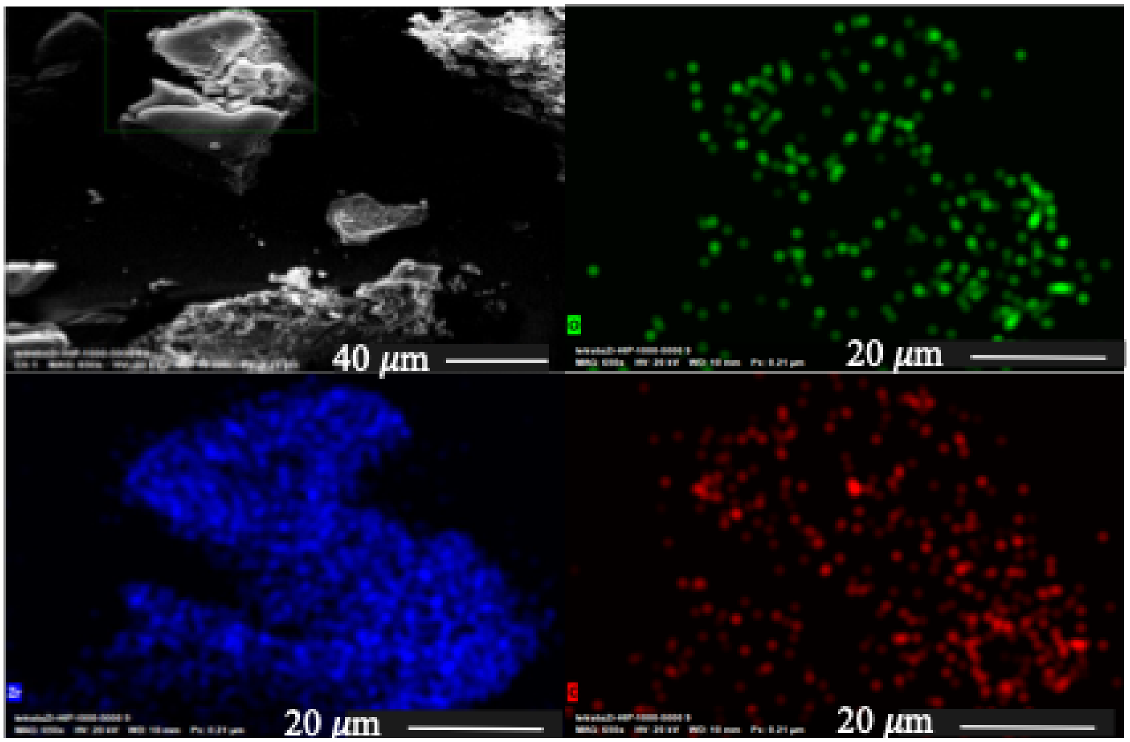

Figure 17. Elemental mapping of product resulting from HIP process of **2**, 1000 °C, 5000 psi, 2 hrs.

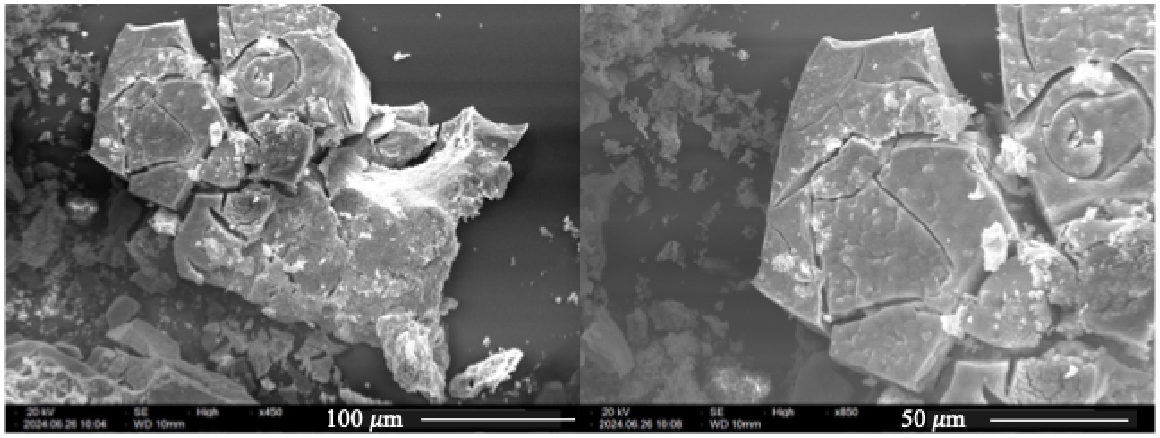

Figure 18. SEM of product HIP process of **2**, 1650 °C, 5000 psi, 2 hrs.

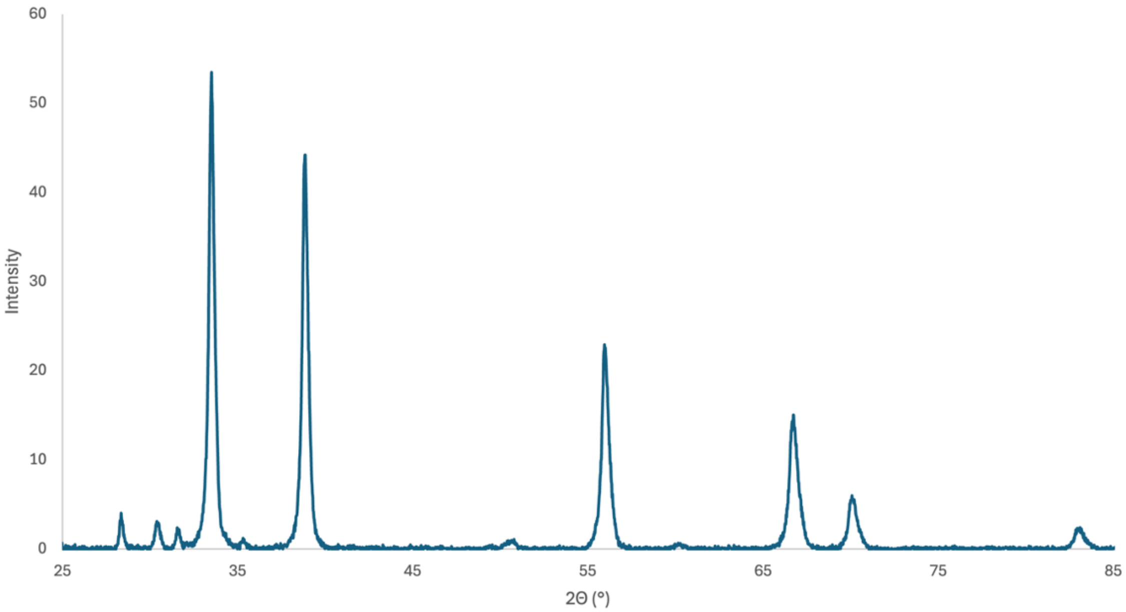

Figure 19. PXRD of product HIP process of **2**, 1650 °C, 5000 psi, 2 hrs. Observed peaks are indicative of ZrC

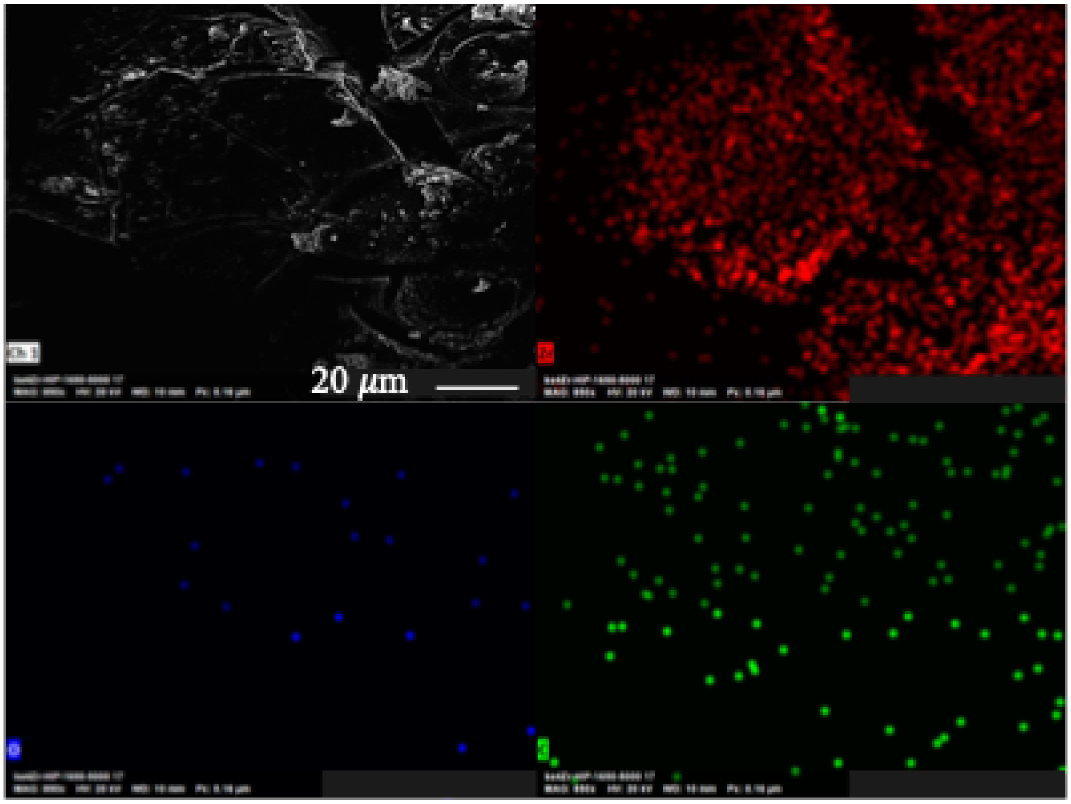

Figure 20. Elemental mapping of product resulting from HIP process of **2**, 1650 °C, 5000 psi, 2 hrs.

Section II: Project Metrics

Grant or Contract Number: N0001424IP00028-Sandia Proposal 018200129
Date Prepared: 11/20/2024
Project Title: Development of Metal Boride/Carbide Precursors for MOCVD Applications
Annual Summary Report: CY2024
Principle Investigator: Harrison D. Root, 505-537-2448, hdroot@sandia.gov; Sandia National Laboratories
Metrics

Number of faculty supported under this project during this reporting period: 3

Number of post-doctoral researchers supported under this project during this period: N/A

Number of graduate students supported under this project during this reporting period: N/A

Number of undergraduate students supported under this project during this period: N/A

Number of scientists / engineers / technicians supported under this project during this reporting period: 3 scientists

Number of refereed publications during this reporting period for which at least 1/3 of the work was done under this effort: N/A

Number of publications (all) during this reporting period: 1 in preparation

Number of patents during this reporting period: N/A

Number of M.S. students graduated during this reporting period: N/A

Number of Ph.D. students graduated during this reporting period: N/A 2 worked on this project, supported by MSIPP program

Awards received during this reporting period:

Invited talks given: N/A

Conferences at which presentations were given (not including invited talks above): N/A

1. Financial information

FY 20xx	**Total Budget**	**Obligated This Period**	**Obligated Cumulative**	**Expended This Period**	**Expended Cumulative**	**Grant/ Contract Period of Performance**
6.1 **(Basic Research Funding)**	**0**	**0**	**0**	**0**	**0**	
6.2 **(Applied Research Funding)**	**0**	**0**	**0**	**0**	**0**	
Total **(if both 6.1 and 6.2 funding was used)**						

2. Administrative notes and other items of interest

- Program welcomed Dr. Matthew Christian to support modeling efforts. Dr. Christian is an early career staff member at Sandia National Lab with extensive experience in DFT modeling.
- Program welcomed the promotion of Dr. Jacob D. Boissiere from postdoctoral researcher to early career staff. Dr. Boissiere will continue to support MOCVD processing thrusts.
- Both Zipporah Harlan and Samaiyah Mason were summer interns supporting this work being supported by Sandia's Minority Serving Institutes Partnership Program (MSIPP).
- Ongoing conversations are underway with Dr. Rebekah Sweat (FAMU) for collaboration opportunities.
- Ongoing conversations are underway with Prof. Babak Anasori (Purdue) for collaborations regarding MXenes
- A commercial MOCVD reactor system has been purchased and we are awaiting delivery in January of 2025.

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