

# Advances in the Development of a $WCl_6$ CVD System for Coating $UO_2$ Powders with Tungsten

Omar R. Mireles<sup>1</sup>, Alyssa Tieman,<sup>2</sup> Jeramie Broadway<sup>1</sup>, and Robert Hickman<sup>1</sup>

<sup>1</sup>NASA Marshall Space Flight Center, Huntsville, AL 35824

<sup>2</sup>Department of Chemical Engineering, University of Alabama, Huntsville, AL 35899  
(256) 544-6327; [omar.r.mireles@nasa.gov](mailto:omar.r.mireles@nasa.gov)

**Abstract.** W- $UO_2$  CERMET fuels are under development to enable Nuclear Thermal Propulsion (NTP) for deep space exploration. Research efforts with an emphasis on fuel fabrication, testing, and identification of potential risks is underway. One primary risk is fuel loss due to CTE mismatch between W and  $UO_2$  and the grain boundary structure of W particles resulting in higher thermal stresses. Mechanical failure can result in significant reduction of the  $UO_2$  by hot hydrogen. Fuel loss can be mitigated if the  $UO_2$  particles are coated with a layer of high density tungsten before the consolidation process. This paper discusses the work to date, results, and advances of a fluidized bed chemical vapor deposition (CVD) system that utilizes the  $H_2$ - $WCl_6$  reduction process.

**Keywords:** Space, Nuclear, Thermal, Propulsion, Fuel, CERMET, CVD, Tungsten, Uranium.

## BACKGROUND

Nuclear Thermal Propulsion (NTP) systems are currently under consideration deep space exploration missions. This enabling technology allows for larger architecture envelope by taking advantage of an improved specific impulse (approximately 850-1000 seconds) that will allow for a much larger range of destinations, shorter trip durations, and improved safety. The reactor fuel must be capable of surviving operation at temperatures between 2850 and 3000 K while exposed the hydrogen working fluid. Establishing technical maturity W-60vol% $UO_2$  CERMET fuel forms that can meet mission service life requirements and risk reduction efforts are major objectives of the program.

## Problem Statement and Objectives

CTE mismatch between W and  $UO_2$  present challenges in addition to the grain boundary structure of W particles. Continuous path contact between fuel kernels can be responsible for the significant reduction of the  $UO_2$  by hot hydrogen ( $H_2$ ). In addition,  $UO_2$  has a high vapor pressure and will be quickly reduced if exposed to the  $H_2$  working fluid leading to fuel loss [1]. Therefore, in order to minimize fuel loss during operation the fuel kernels are coated with a high density layer of tungsten. The objective of this project is to advance a lab-scale prototype that utilizes the  $WCl_6$  reduction process to coat spherical  $UO_2$  powders with 40 vol% tungsten leaving minimal Cl contamination. Coated spherical powders are also advantageous for HIP consolidation process in that there will be minimal powder segregation during fill and will yield a higher green powder packing density. Operating experience of the CVD system over the last year has revealed several areas of processing improvement, particularly in the prevention of inadvertent feed-line blockage in the reactor manifold consisting of  $WCl_6$  and tungsten coated  $ZrO_2$  powder. This document details ongoing CVD development efforts at NASA Marshall Space Flight Center (MSFC).

## APPARATUS AND PROCEDURE

The CVD system consists of a fluidized bed, raining feed concept that is designed to mitigate contamination concerns. Argon (Ar) carrier gas from a dewar and H<sub>2</sub> fluidization/reaction gas from a k-bottle are regulated using two Alicat Scientific MDR-500SLPM-D mass flow controllers. A H<sub>2</sub>/Ar ratio of 10:1 is maintained to achieve the appropriate reaction stoichiometry [2]. Gases are then heated to 230 °C using an Omega AHPF-121 circulation heater before introduction into the sublimator and the reactor. Approximately 25 g of spherical powder (38 to 100 μm diameter) is fed into the reactor by actuating a Swagelok pneumatic pinch valve mounted on top of the expander, where the powders enter the reactor and achieve a fluidized state. Approximately 10 g of WCl<sub>6</sub> reagent powder is loaded into a test tube within a dry atmosphere glove box and transferred to the Pyrex sublimator that encloses a medium frit on which the powder rests. The sublimator walls are heated by HTS/Amptek electrically heated jackets to between 160 to 200 °C in order to induce sublimation of the powder and produce the reagent vapor. Heated Ar flows through the sublimator and transports the WCl<sub>6</sub> vapor to the reactor manifold. The AG Scientific Glass quartz reactor consists of a manifold where the H<sub>2</sub> and WCl<sub>6</sub> vapor mix, fluidization column, and glass to metal transition seal. Gas heaters, heating jackets, and the furnace temperatures are maintained with PID controllers coupled to type-K thermocouples. The reactor is surrounded by a Mellen clamshell electrical furnace and heated to 930 °C (900 °C at the reactor fluidization column) to induce H<sub>2</sub> reduction of WCl<sub>6</sub> as shown in equation 1.



Tungsten deposition on the dUO<sub>2</sub> substrates occurs uniformly due to the fluidized nature of the powders. Exhaust gases flow out of the Inconel 600 expansion vessel, through 0.5 μm filters to retain fine powders, through an acid trap to retain HCl vapor, then directed to the resistively heated SiC filament to burn-off the H<sub>2</sub>. Coating thickness is controlled by varying the sublimator reaction time, which typically ran 30 to 60 minutes in duration. After a coating run, the sublimator heater and furnace are deactivated to terminate the deposition reaction while the powders continue to fluidize until they reach approximately 100 °C. Gas flows are terminated and the powders settle at the bottom of the Pyrex collection hopper, which is disconnected from the CVD system, transported to an inert glove box.

### System Improvements

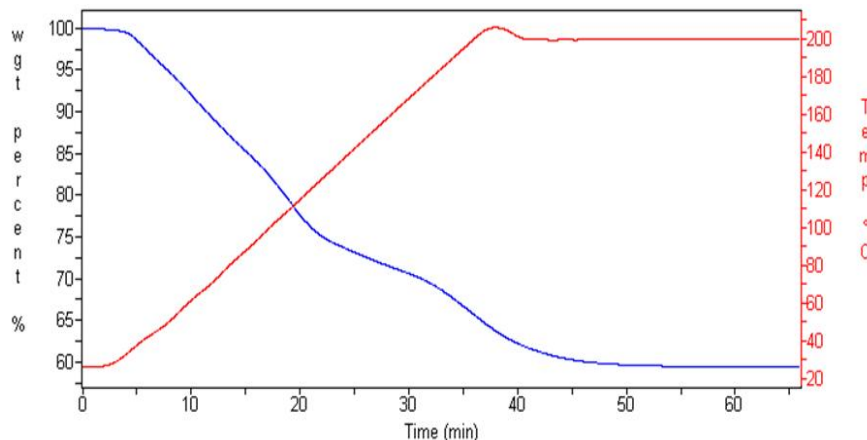
Numerous improvements were integrated into the CVD system based on operational experience. Gas supply lines were simplified by utilizing welded components that removed unnecessary valves and fittings. Process variable control and monitoring improved through a computer-based the implementation of a data acquisition and control system. Bellows were installed after gas heaters to allow for thermal expansion for line compression during the evacuation process. Viton o-rings were replaced with Markez Z1028 o-rings capable of increased service life in the corrosive environment up to 300 °C. The reactor design was optimized by utilizing an all quartz construction, increased wall thickness, and ball-socket joints with Apiezon-H grease to create an effective seal yet also have misalignment tolerance. The H<sub>2</sub> burn-stack flame arrestor was changed to a Nichrome mesh that greatly increasing service life. For improved operational safety an H<sub>2</sub> ScanCorp HY-ALERTA H<sub>2</sub> area monitor was installed over the system and integrated with the control system to close a solenoid operated valve in the event that a leak increased H<sub>2</sub> quantities to beyond shut-down limits. Using results from an empirically benchmarked model the expander length was decreased by nearly 27 cm, while still retaining performance properties. The new expander design also utilized a corrosion resistant Inconel 600 construction and decreased the number of required fittings. A substantial number of procedural changes were also implemented based on operational experience. These updated procedures greatly decrease the probability of off-nominal behavior and impose practical engineered solutions to improve safety.

### Optimization of WCl<sub>6</sub> Sublimation Rate

Previous CVD runs revealed that there was insufficient WCl<sub>6</sub> vapor yield to coat powders in a reasonable operating period. Powders showed very thin coatings even after long run times, which could render the process non-economical if left uncorrected. The sublimation temperature of 200 °C was based on literature reviews and not on contemporary empirical data [3]. Therefore, an effort was initiated to characterize WCl<sub>6</sub> vapor yield as a function of temperature and carrier gas flow rate in order to optimize vapor yield and consequently coating deposition rate.

### *Sublimation Rate Using Thermo-Gravimetric Analysis*

Weight curves as a function of temperature were obtained by using a Thermo-Cahn Versa-Therm Thermo-Gravimetric Analyzer (TGA). Approximately 5 mg of  $WCl_6$  was placed in a platinum pan/gondola and heated at a rate of 5 °C/minute to 200 °C in a nitrogen atmosphere. Once at temperature, the sample continued to be heated for 30 minutes. An example of a TGA weight curve and heating schedule is shown in Figure 2.



**FIGURE 2.** TGA curve of  $WCl_6$  heated to 200 °C at 5 °C/minute in nitrogen.

TGA results were used to estimate the onset of sublimation at between 33 to 35 °C, although the vapor yield was very low at these temperatures. A second, more prominent inflection point occurred between 101 to 105 °C, which slightly decreased the vapor yield. The sublimation rate increased again at approximately 188 °C then stabilized when the temperature was held at 200 °C. Unfortunately, after several runs there was some disagreement between data and it was decided that sufficient initial results were obtained to warrant a series of tests using the CVD system.

### *Sublimation Rate Using the CVD System*

It was observed on prior CVD runs that the  $WCl_6$  precursor powder sublimated at regions near the sublimator wall but not near the frit center-line on which the powder rested resulting in an untouched mound of  $WCl_6$  powder. One likely reason for this behavior would be non-uniform temperature distribution within the sublimator frit. In order to better characterize the thermal environment the sublimator was fitted with a series of type-k thermocouples at the sublimator inlet, frit centerline, sublimator outer wall adjacent to the frit, sublimator outlet, and at the re-designed reactor manifold. The new reactor manifold used a coarse frit at the  $H_2/WCl_6$  vapor junction to prevent inadvertent depositing of  $dUO_2$  powder within the vapor feed line. During operational trials it was noticed that the temperature of the sublimator wall followed that of the external band heater surrounding the sublimator as expected. However, it was discovered that the frit center-line was up to 30 °C cooler than the heated wall accounting for the mound of  $WCl_6$  powder at the frit center-line. Subsequent data analysis revealed that the frit center-line temperature closely followed the sublimator inlet temperature which was effectively being cooled by the Ar carrier gas which had an average temperature of 25 °C. In addition, the reactor manifold was also being cooled by the  $H_2$  fluidization gas also at 25 °C. The combination an unheated wall and low gas temperatures were responsible for deposition of  $WCl_6$  at the reactor manifold and consequently resulting in blockage. Therefore, it was decided that both the carrier and fluidization gases required heating prior to entering the sublimator and reactor, respectively. Electrical gas heaters were installed upstream of the sublimator and collection hopper to heat the argon and  $H_2$  to 230 °C. In addition, external jacket heaters were installed around the reactor manifold and powder collection hopper to prevent unwanted  $WCl_6$  plating out on these surfaces. Subsequent temperature characterization runs showed marked improvement in the temperature uniformity of the heated regions of the CVD system. A bore-scope was installed on the wall of the sublimator in order to observe the behavior of the  $WCl_6$  powder as a function of temperature. These visual observations helped to validate many hypotheses and some of the TGA findings with regards to powder behavior inside the sublimator during heat up and operation.

During one run a fluffy yellow deposit formed within the sublimator and clogged the reactor manifold frit. It was later determined that the temperature of the manifold frit was not at the nominal operating temperature of 210 °C before sublimation was initiated. In addition, the deposit was likely the result of reaction with water or alcohol absorbed within the frit. After each run the sublimator was thoroughly cleaned to remove all traces of  $WCl_6$  and air dried overnight. Absorbed volatiles in the frit reacted with the  $WCl_6$  upon heating resulting in the deposit. The clog was further exacerbated by initiating sublimation before the reactor manifold frit was above 210 °C leading to  $WCl_6$  deposition on the frit. As a result the sublimator is now baked after cleaning at 150 °C for 1 hour to drive off volatiles, and then cooled overnight in a low-moisture desiccator. The sublimator is installed in the CVD, loaded with powder immediately before operation, evacuated, purged, and then the reactor manifold heated to 210 °C before initiating sublimation. These steps have proven effective in preventing undesired deposition along the carrier gas flow path.

A coarse method to estimate  $WCl_6$  utilization was to measure the weight of powder loaded into the sublimator before a sublimation trial then measure the weight of remaining powder after the trial. Knowing the change in mass and the time at temperature allowed for the determination of an average sublimation rate. Several sublimation trials were carried out with initial  $WCl_6$  loadings varying from 5 to 10 g and temperature ranges from 160 to 230 °C. The data from these sublimation trials culminated in a graph that depicts the average sublimation rate as a function of temperature as shown in Figure 3. From this graph we see that maximum vapor yield occurs at about 200 °C.

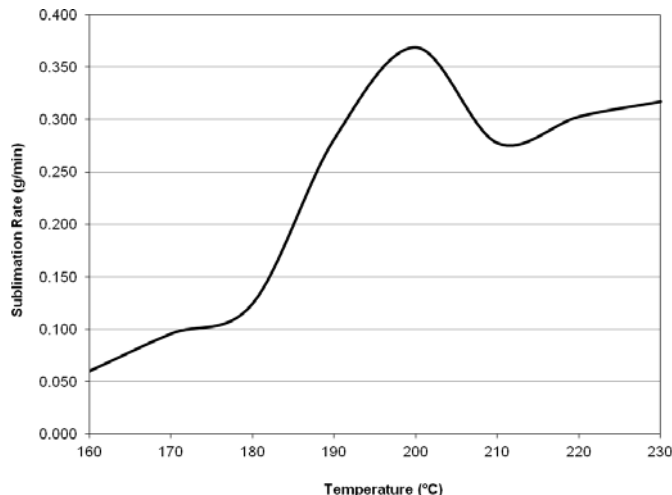


FIGURE 3. Sublimation rate of  $WCl_6$  powder as a function of temperature.

## Materials Compatibility Study

Standard glass-to-metal transition seals are constructed of Pyrex or quartz and 304 SS. Experience gained in operational trials of the CVD demonstrated that significant corrosion of stainless steel components was occurring. Corrosion products would later manifest themselves as contaminants mixed with the coated powders. Even trace quantities of contaminants in the powder feedstock can result in the formation of eutectics during the HIP process or a potential failure initiation inclusion during NTP operation. Therefore, a more corrosion resistant material was needed in the glass-to-metal seals to replace 304 SS. A thorough literature review was conducted and four materials emerged as possible candidates: Hastelloy C-276, Inconel 600, Inconel 718, and Titanium 6-4. Tube (diameter 12.7 mm, wall thickness 0.889 mm) was acquired in order to produce a series of material coupons for testing.

### *CVD System Corrosion Resistance*

Small coupons of each candidate material were placed directly in the sublimator and expander regions of the CVD system to expose the coupons to expected operational conditions as shown in Figure 4.

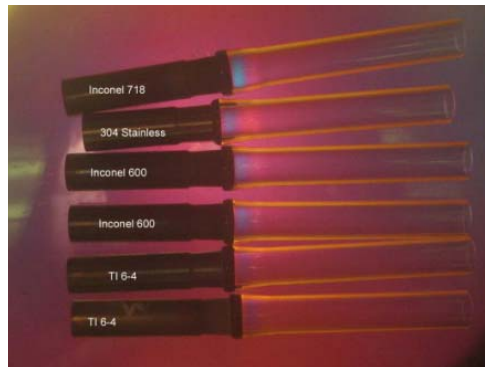


**FIGURE 4.** Material candidate samples in the sublimator before and after CVD operation.

Photographs, weight and dimensions of each sample were obtained before and after exposure tests in order to quantify changes. Results show that there was negligible change in surface finish, weight, or dimensions for samples exposed in the expander. Samples exposed within the sublimator showed similar behavior with the exception of Titanium 6-4 which showed a slight increase in weight of <1%, which was verified by visible formation of scale on the surface. It was observed that there was significantly less  $WCl_6$  utilization in regions adjacent to the metal samples and scale developed on the samples. These results indicate that it would be advantageous to continue using Pyrex as the sublimator material of construction.

#### *Glass-to-Metal Seal Suitability*

Larson Electronic Glass was provided with tube samples to evaluate the feasibility of candidate materials to produce glass-to-metal transition seals that would meet the 304 SS industry standard. Seals were created using the tubes then subjected to a battery of tests to evaluate performance. First, samples were torch annealed on a glass lathe and vacuum leak tested. Samples were oven heated and imaged using a polarized filter to observe seal strain as shown in Figure 5. Samples were frozen then immersed in hot water to observe thermal shock behavior. Finally, the samples were cleaned to attempt removal of surface oxide layers. Test results are shown below in Table 1.



**FIGURE 5.** Polarized image of the heat induced strain on the glass-to-metal seals. *Image courtesy of Larson Electronic Glass.*

**TABLE 1.** Material Candidate Performance Results. *Data courtesy of Larson Electronic Glass.*

Sample	Seal	Strain	Strain (rel. 304SS)	Thermal Shock	Cleaning
Hastelloy C-276	Fail	Fail	Greater	N/A	N/A
Inconel 600	Good	Low	Lower	Minor separation	Good result
Inconel 718	Good	Low (> Inc. 600)	Lower	Fail	N/A
Titanium 6-4	Good	Low	Lower	No change	Abrasive required

C-276 was quickly removed from the candidate list as it mechanically failed shortly after formation of the seal. When heated the strain field within the seal was observed and it was noted that three of the candidate materials exhibited lower strain than the standard 304 SS. Inconel 718 was eliminated due to failure during thermal shock tests. It must be noted that Inconel 600 showed some minor internal separation but that behavior is normal even for 304 SS. Inconel 600 cleaned easily while Titanium 6-4 was unsuccessful without the application of abrasives. Based on the performance test results conducted at Larson/MSFC, weldability, and lower cost Inconel 600 was selected over Ti 6-4. It was decided that the sublimator would retain Pyrex for material of construction while expander and all metal-to-glass transitions would be fabricated of Inconel 600.

## CVD SYSTEM PERFORMANCE RESULTS

Control and performance of the upgraded CVD system was evaluated through a series subsystem and fully integrated system shake-out trials. The numerous temperature zones behaved as expected, sublimation yield showed significant improvement, and powders were coated for a short trial period. Soon after the coating trial began it was noticed that the dark tungsten deposit became opaque much quicker than on previous runs and the system pressure showed a slight increase. Post-run inspection showed that there an opaque dark powder deposit on the reactor wall and in the exhaust filters. The dark powder was tungsten and the large quantity was due to the sublimator operating at the optimal sublimation temperature. Although optimized from a vapor yield standpoint the amount of  $WCl_6$  vapor produced was excessive for the CVD system to efficiently utilize during the coating process. Tungsten that was not utilized in the powder coating process deposited on the reactor wall and in the exhaust filters. As a result, operating procedures were modified to optimize the vapor yield so that a steady tungsten deposition rate can be controlled as a function of a lower sublimation temperature. Powders from these trial run showed noticeable deposition and microstructural characterization of the powders was initiated after each run. SEM micrographs show that the powders are indeed developing a thin yet uniform coating. Figure 6 and 7 show the coating of a  $ZrO_2$  particle after a 15 minute deposition period.

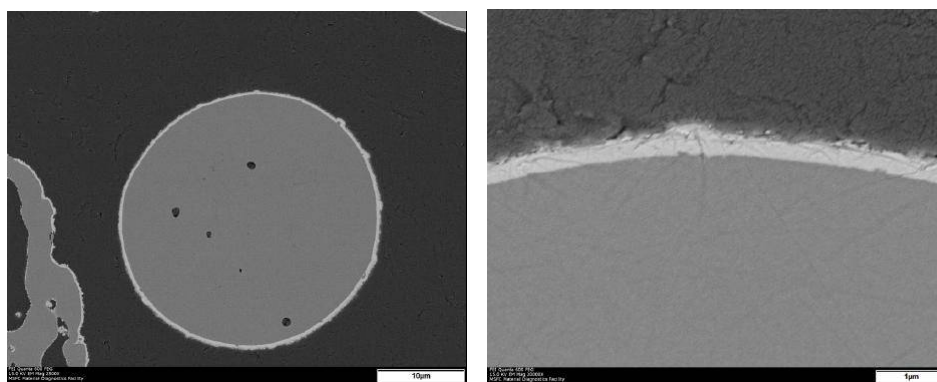


FIGURE 6 & 7. SEM micrographs of tungsten coated  $ZrO_2$  powder at 2,500x and 20,000x.

EDS analysis show that chloride based contaminants are on the order of a few percent before contaminant removal in a  $H_2$  furnace. At the time of writing this document the CVD system was continuing to be operated using  $ZrO_2$  surrogate powders in preparation to a switch to  $dUO_2$  powders within a few months.

## CONCLUSIONS

The iterative development process has demonstrated the feasibility of coating powders with tungsten using the  $WCl_6$  process. Although initial coating thicknesses are thin they are easily increased with additional deposition run time. More importantly, the lack of significant quantities of impurities within the coatings indicates that this process will be capable of meeting NTP coated powder requirements. In addition, efforts are ongoing to produce coated powders with the appropriate coating density, adhesion, thickness, and grain boundary orientation based on reference design concepts and requirements. Routine operation of the  $WCl_6$  based CVD system that yields expected quantities of appropriately coated powders will overcome one of the major obstacles to the successful fabrication and implementation of W- $UO_2$  cermet fuel forms for NTP application.

## RECOMMENDATIONS FOR FUTURE WORK

Significant progress has been made in the development of the CVD system. However, several tasks remain before the process can be confidently brought to bear on NTP fuel development. Items remaining include optimization of process variables in order to produce coating properties that meet requirements and improved coating characterization as a function of substrate microstructure and process variables.

## NOMENCLATURE

Ar = Argon  
°C = degree Celsius  
CTE = Coefficient of thermal expansion  
CVD = Chemical Vapor Deposition  
dU = depleted uranium  
EDS = Energy Dispersive Spectroscopy  
g = gram  
H<sub>2</sub> = hydrogen  
HIP = Hot Isostatic Press  
K = degree Kelvin  
MSFC = Marshall Space Flight Center  
SEM = Scanning Electron Microscope  
SiC = Silicon carbide  
SS = stainless steel  
SLPM = standard liter per minute  
vol% = volume percent  
WCl<sub>6</sub> = Tungsten hexa-chloride  
UO<sub>2</sub> = Uranium di-oxide  
μm = micrometer  
ZrO<sub>2</sub> = Zirconium di-oxide

## ACKNOWLEDGMENTS

The authors would like to thank Grace Belancik, Richard Booth, David Bradley, Philip Brown, Roger Harper, Adam Kimberlin, Zachary Koch, James Martin, Stan McDonald, Timothy Nelson, Eric Osborne, Ronald Renfroe, Eric Stewart and Frank Zimmerman of NASA Marshall Space Flight Center; Gene Nelson of AG Scientific Glass, and Chuck Larson of Larson Electronic Glass for their effort and support. The NASA Nuclear Cryogenic Propulsion Stage (NCPS) project supported the work described in this report as part of technology development and evaluation activities. Any opinions expressed are those of the author and do not necessarily reflect those of NASA.

## REFERENCES

- <sup>1</sup>Grisaffe S. and Caves R. M., *NASA TM X 1028*, 1972/
- <sup>2</sup>Mireles, O., et al., "Development of a Fluidized bed CVD System for Coating UO<sub>2</sub> particles with Tungsten," in *Proceedings of Nuclear and Emerging Technologies for Space Symposium*, LPI Conference Proceedings, Houston, Texas, 2012, paper 3021.
- <sup>3</sup>Oxley, J.H., et al., "Coating Uranium Dioxide Powders with Tungsten," *Journal of Industrial and Engineering Chemistry*, Vol. 51, No. 11, 1959, pp. 1391-1394.