Advances in the Development of a WCl$_6$ CVD System for Coating $UO_2$ Powders with Tungsten

NASA Advanced Exploration System (AES) Project: Nuclear Cryogenic Propulsion Stage

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• NTP fuels under development
  − W-60vol%UO₂ CERMET

• Minimize erosion
  − Prevent H₂ propellant (2850-3000 K) from reducing UO₂ fuel kernels
  − Clad each fuel kernel in tungsten

• Coat spherical dUO₂ powders with 40 vol% W

• Coated spherical powders advantageous for HIP
  − Higher powder packing %TD
  − Minimize powder segregation
Problem & Objectives

- WF$_6$ process
  - Residual F exacerbates fuel loss
  - HF bi-product

- WCl$_6$ process
  - Minimal Cl contamination
  - More complex than WF$_6$ process (solid-to-vapor vs. gaseous reagent)

- Vendor cost to coat dUO$_2$ excessive

- Develop a lab-scale prototype that utilizes the WCl$_6$ process that enables cost effective coating of spherical dUO$_2$ powders
CVD Apparatus & Procedure

- **WCl₆ process**
  - Fluidized bed reactor
  - Raining feed system
  - H₂/Ar 10:1 ratio
  - 25 g batches
  - 30 to 60 min

\[
\text{WCl}_6 + 3\text{H}_2 \rightarrow \text{W} + 6\text{HCl} + \text{Ar} + x\text{s} \text{H}_2
\]
CVD Results

CVD Run 4: 60 minutes. W coated ZrO2, average particle OD 31.0 μm, average coating thickness 1.76 μm.

CVD Run 5: 30 minutes. W coated ZrO2.
Performance Improvement

- Vapor yield optimization
- Flow Line Blockage
  - Indications of temperature dependence
  - Continued blockage results in line leakage
- Component optimization
- Materials optimization
- System control and monitoring

H₂ and WCl₆/Ar mixture junction at reactor inlet
Sublimer outlet line blockage
WCl₆ and W coated ZrO₂ blockage
Sublimer outlet ball joint vacuum grease blow by location
Sublimer Characterization & Optimization

- Increase WCl₆ vapor yield
- Determine min/max sublimation temperatures
- Characterize yield vs. temp and carrier gas flow rate
- Optimize WCl₆ vapor yield

<table>
<thead>
<tr>
<th>T₀°C (°C)</th>
<th>t (min)</th>
<th>Vial No</th>
<th>Mᵣ (g)</th>
<th>Mᵣ-WCl₆ (g)</th>
<th>M₀-WCl₆ (g)</th>
<th>Initial M₀-WCl₆ (g)</th>
<th>ΔM (g)</th>
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<tbody>
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<td>160</td>
<td>30</td>
<td>1</td>
<td>16.0</td>
<td>21.1</td>
<td>5.1</td>
<td>2.6</td>
<td>2.5</td>
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<td>170</td>
<td>30</td>
<td>2</td>
<td>15.9</td>
<td>21.1</td>
<td>5.2</td>
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<tr>
<td>180</td>
<td>30</td>
<td>3</td>
<td>15.6</td>
<td>21.0</td>
<td>5.4</td>
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<td>30</td>
<td>4</td>
<td>15.9</td>
<td>21.0</td>
<td>5.1</td>
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<td>200</td>
<td>30</td>
<td>5</td>
<td>16.0</td>
<td>21.2</td>
<td>5.2</td>
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<td>210</td>
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<td>6</td>
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<td>20.9</td>
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<td>15.7</td>
<td>21.0</td>
<td>5.3</td>
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<td>230</td>
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<td>8</td>
<td>15.6</td>
<td>20.8</td>
<td>5.2</td>
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</table>
Sublimer Temperature Profiles

Argon pre-heater only

Sublimer heat tape only

Argon pre-heater and heat tape

PID set-points for desired sublimer frit centerline temp.
Sublimer Characterization: 160 °C Run

- Sublimer Temperature Profile
- Sublimer (post test)
- Sublimer outlet line (post test)
- Sublimer outlet frit 1 up stream (post test)
- Vacuum cryo trap (post test)
Failed run due to “cotton candy” blockage.

Blockage a function of temperature schedule and entrained volatiles (cleaning solutions and water)

Sublimer are now baked to 150 °C for 1 hour to drive off volatiles in the frit immediately before a run.

Reactor manifold frit should be maintained above 210 °C to prevent blockage.
Sublimer Characterization: TGA

- Observation of sublimation inflection points using Thermal Gravimetric Analysis (TGA)
- Objective: Quantify WCl₆ onset sublimation temperature and sublimation rate

Conclusion: Sublimation onset at 33-35 °C, 101-105 °C, and 188 °C. Retained 200 °C nominal temperature.
Based on coarse sublimer characterization data

Higher fidelity rates obtained using TGA

CVD runs at 200 °C exhibited excessive vapor yield

160 °C selected as optimal sublimer frit center-line operating temperature
• Assumptions
  – Ar & H2 flow-rates 1 & 10 SLPM respectively
  – Gas mixture enters at 200 °C and 20 psia
  – Glass surface temperature of 900 °C
  – Furnace starts at ~ 5” and ends at 17”
  – Axial conduction through the glass is neglected

• Results
  – Gas at low flows, through un-insulated glass, is rapidly cooled by outside
  – No thermal reason for expander
  – Particle velocity reason for expander (retain fines)

• Conclusion: Reactor and expander sections too long. Shorten reactor 4 inches, shorten expander 10.5 inches.
Materials Compatibility Study

- Glass (Pyrex/quartz)-to-304 SS seals
  - Significant corrosion in CVD environment
- Corrosion resistant candidate materials
  - Ti 6-4, Inconel 600, Inconel 718, Hastelloy C-276
- Exposed coupons in sublimer and expander
- Larson Electronic Glass provided with material samples to determine seal suitability
  - Samples torch annealed on a glass lathe
  - Seals frozen then immersed in hot water
  - Heated in oven to observe strain
  - Cleaning (removing oxide layer from metal)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Seal</th>
<th>Strain Test</th>
<th>Strain (rel. to 304 SS)</th>
<th>Thermal Shock Test</th>
<th>Post Test Cleaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hastelloy C-276</td>
<td>Fail</td>
<td>Fail (fell apart)</td>
<td>Higher</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Inconel 600</td>
<td>Good</td>
<td>Low</td>
<td>Lower</td>
<td>Minor internal separation (like 304 ss)</td>
<td>Cleaned up well</td>
</tr>
<tr>
<td>Inconel 718</td>
<td>Good</td>
<td>Slightly &gt; Inconel 600</td>
<td>Lower</td>
<td>Fail (fell apart)</td>
<td>N/A</td>
</tr>
<tr>
<td>Titanium 6-4</td>
<td>Good</td>
<td>Low</td>
<td>Lower</td>
<td>No change</td>
<td>Unsuccessful without abrasive</td>
</tr>
</tbody>
</table>

- Inconel 600 selected over Ti 6-4 due to corrosion resistance, weldability, and cost
- Sublimer will remain Pyrex while expander and metal-to-glass transitions made of Inconel 600
CVD Upgrades

- Gas line simplification, valve sequence, ball/socket joints
- Pneumatic powder fill pinch valve
- Ar & H₂ pre-heaters
- Collection Hopper
- Burn-stack hinge & nichrome flame arrestor
- H₂ and Ar Reactor Inlet Bellows
- Markez Z1028 O-rings
- Inconel 600 Expander (optimum height)
- Inconel 600-to-Quartz Reactor Seals
- H₂ Area Monitor
- Lexan Containment
- DAQ System
- Manifold Filter
- Heating Jackets
- Sublimer Bore Scope
• Demonstrated viability and utilization of:
  - Fluidized powder bed
  - WCl₆ CVD process
  - Coated spherical particles with tungsten

• The highly corrosive nature of the WCl₆ solid reagent limits material of construction

• Indications that identifying optimized process variables with require substantial effort and will likely vary with changes in fuel requirements
Future Work

• Optimize process variables in order to produce coating properties that meet requirements

• Characterize coatings as a function of substrate microstructure and process variables

• Design CVD system to process large quantities of power required for engine scale fuel fabrication
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