Development Status of a CVD System to Deposit Tungsten onto UO_2 Powder via the WCl_6 Process

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

NETS
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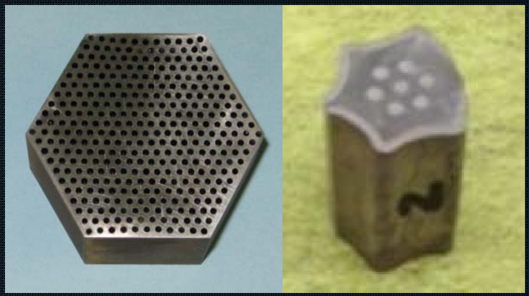
Background

- NTP fuels under development
  - W-60vol%UO_2 CERMET
  - Fuel loss through erosion
  - Inherently stable W fuel element cladding
  - Coat spherical UO_2 fuel kernels in 40 vol% W



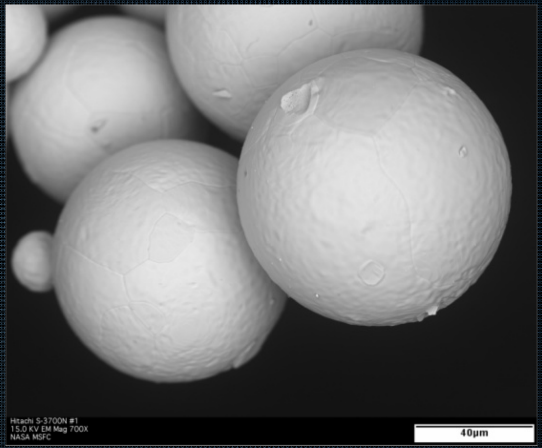
331 and 7 channel fuel samples

- Performance Advantages
  - Prevent H_2 propellant at 2850 K from reducing UO_2 fuel kernels
  - Minimize erosion and fuel loss

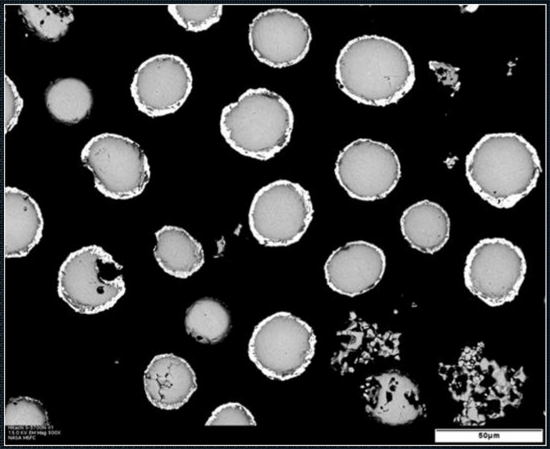
- Manufacture Advantages
  - Excellent powder distribution uniformity during HIP can fill
  - Prevents segregation during HIP can fill
  - Higher green packing density
  - Minimize dimensional distortion during HIP

Problem & Objectives

- Vendor cost to coat dUO_2 in W excessive
- WF_6 process
  - Industry standard for W deposition
  - Gaseous reagent
  - Excessive F contamination in UO_2 substrate and W coating
  - Residual F exacerbates fuel loss
- WCl_6 process
  - No UO_2 chlorination with WCl_6 or reaction products
  - W coatings do not excessively contaminate substrate
  - WCl_6 preferable to WF_6 for coating UO_2 with W
  - More complex (solid-to-vapor reagent gas)
  - Not an industrially utilized process
- Develop a lab-scale prototype that utilizes the WCl_6 process that enables cost effective 40vol% coating of spherical dUO_2 powders



SEM micrograph of uncoated UO_2 sol-gel particles (700x)



SEM micrographs of spherical W-coated ZrO_2 particles

Coating Requirements

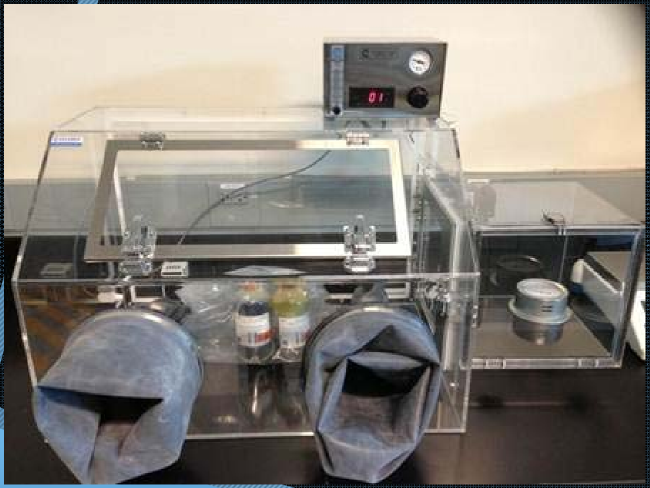
- Fully encapsulate UO_2 substrate
- Thickness: 40 ± 1 vol%, uniform spatial distribution
- Density: pore-free, > 18.7 g/cm^3 - 19.2 g/cm^3
- Purity: > 99.98% W, ≤ 10 ppm impurities
- Process: must not react with UO_2 substrate
- Adhesion: must not de-bond, spall, crack or blister up to 3000 K
- UO_2 fuel loss: <1.9 wt% (<1 mg/cm^2) when heated to 3000 K in flowing H_2 for 2 hours

Apparatus

- WCl_6 process
  - Temperature: 950°C (higher results in large columnar grains
  - H_2/WCl_6 mole ratio: 10:1 to 30:1
  - Pressure: < 10 mm Hg (0.193 psia)

$$WCl_6 + 3H_2 \xrightarrow{Ar,\, xs\, H_2,\, 930^\circ C} W + 6HCl + Ar + xs\, H_2$$

- CVD System
  - Fluidized bed reactor
  - Raining feed, 25 g batches
  - 20 to 60 min



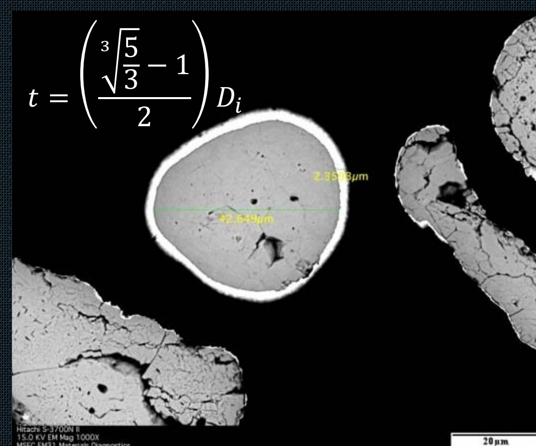
CVD System

Spouted Reactor

- Accomplishments
  - Fluidization of ZrO_2
  - Coating ZrO_2 to 60% of target thickness in 20 minutes
  - Demonstrated viability of the WCl_6 CVD process
  - Coating spatial uniformity (thickness measured through cross section examination)
  - Path: ZrO_2, HfO_2, UO_2

Spouted reactor design. Fluidization pre & post deposition process

- Limitations
  - Powder drop-out: difficult to fluidize HfO_2 without high H_2 flow rates & powder small quantities
  - Complex design
  - Fragile and expensive glass-metal transition



$$t = \left(\frac{\sqrt[3]{\frac{5}{3}} - 1}{2} \right) D_i$$

ZrO_2, $D_{p,u}$ = 42.649 μm, 20 min run, t = 2.3593 μm, (59.6% of goal) Deposition rate = 7.078 μm/hr

ZrO_2, $D_{p,\,u}$ = 14.519 μm, 20 min run, t = 2.1184 μm (157.2% of goal) Deposition rate = 6.3552 μm/hr.

Fluidization

- Calculate fluidization conditions
  - Estimate Reynolds number and terminal velocity of powders in a fluidized state.
- Empirical data
  - Develop correlations based on empirical data
  - Verify correlations with observed fluidization behavior
- Reactor estimation
  - Extrapolate calculated and empirical results to estimate minimum fluidization flow rate
  - Reactor design and particle specific

Powder	Theoretical Density (g/cm^3)	Actual Density (%TD)	Particle Size (µm)
ZrO_2	5.68	50	53 - 106
HfO_2	9.68	99	100 – 200
UO_2	10.97	99	50 – 150

$$Re_{mf} = (29.5^2 + 0.375Ar)^{1/2} - 29.5$$

$$Ar = \frac{gD_p^3\rho_f(\rho_p - \rho_f)}{\mu_f^2}$$

$$V_T = \frac{2gD_p^2(\rho_p - \rho_f)}{18\mu_f}$$

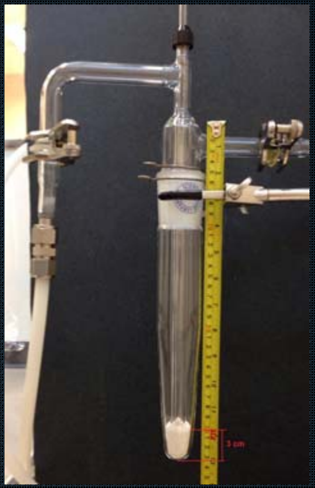
- Re_{mf} = Reynolds number for minimum fluidization (sphereicity > 0.93)
- Ar = Archimedes number
- g = gravity
- D_p = particle diameter
- ρ_p = particle density
- ρ_f = fluid density
- μ_f = fluid viscosity
- V_T = particle terminal velocity

Inverted Reactor

- Fluidization Prototype
  - Simplified & robust design
  - Based on lessons learned
  - Co-centric fluid lines
  - Built and tested

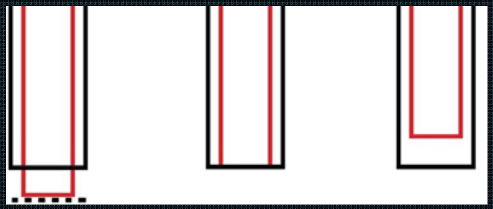
- Fluidization
  - HfO_2 (30, 60, 100, 200 g)
  - Room temperature argon
  - Fluidization vs. flow rate
  - Inner/outer fluidization line
  - Straight vs. tapered reactor wall
  - Fluidized column height behavior
  - Determined minimum and optimum fluidization flow rates
  - Data used to design inverted CVD reactor

Inverted Reactor Prototype (straight)



Inverted Reactor Prototype (tapered)

Fluidization: Tapered, 103 g HfO_2, Ar, 30 L/m outer, 1 L/m inner, flush.

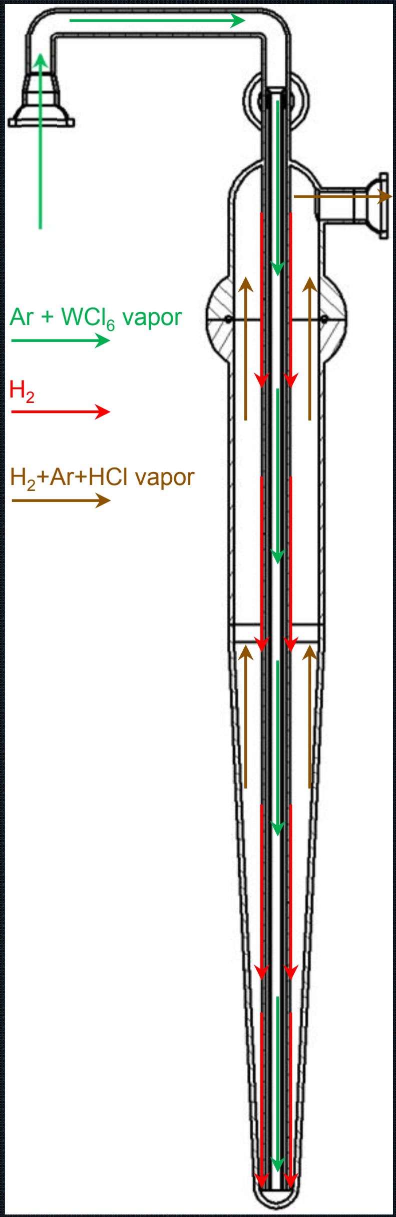


Co-centric tube positions

Powder loading and fluidization vs powder mass

Inverted Reactor Geometry

- Reactor manifold
  - Pyrex
  - Co-centric reactant and fluidization lines
  - Ball-socket gas connections
- Reactor Wall
  - Quartz
  - Tapered
  - Contains powder, eliminates powder drop out collection hopper
- Reactor O-ring Joint
  - Standard item
  - Eliminates glass-to-metal transitions
  - Thicker walls = robust
- Inverted Reactor
  - UO_2 fluidization and coating trials in March

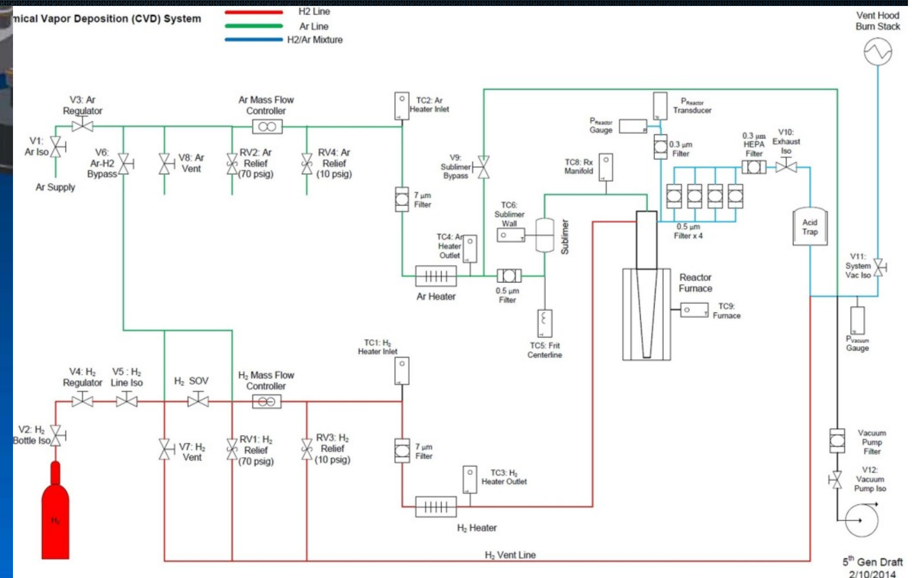


Inverted Reactor Design

Additional CVD Upgrades

Inverted reactor sublimer

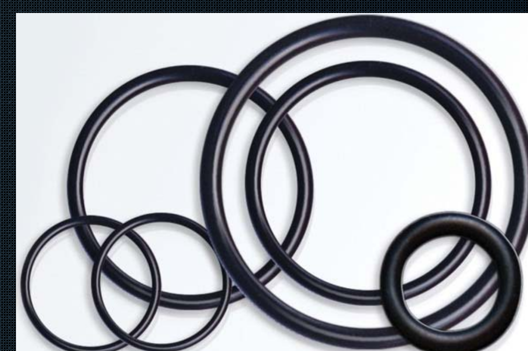
Inverted Reactor System Layout



Gas line simplification, fitting/valve reduction

Data Acquisition and Control System

Reactor handling glove box.



Kalrez 4079 O-rings

Conclusions

- Demonstrated viability of the WCl_6 CVD process to coat ZrO_2 particles with W.
- Inverted reactor designs are far more forgiving and robust than spouted designs.
- Corrosive nature of WCl_6 vapor limits reactor material to Inconel, pyrex, quartz.
- Transition from surrogate to dUO_2 powder as quickly as possible in order to address changes in process variables specific to dUO_2.

Recommendations for Future Work

- Optimize process variables
  - WCl_6 powder, H_2, Ar impurity content
  - Reactor temperature
  - Reactor heat/cool rates
  - H_2/WCl_6 mole ratio
  - Flow rates as a function of coating thickness
  - Deposition rate as a function of particle size

- Coating characterization
  - Thickness
  - Spatial uniformity
  - Impurity content
  - Adhesion
  - Micro-hardness
  - Surface roughness
  - Grain structure (epitaxial content, grain orientation)
  - Grain orientation effect on coating properties (heat transfer/diffusion)
  - Grain boundary population impact on fuel retention

- Potential H_2 heat treatments
  - Pre-deposition to clean substrate surface: effect on coating adhesion
  - Post-deposition to remove impurities: effect on W grain growth

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