DEVELOPMENT STATUS OF A CVD SYSTEM TO DEPOSIT TUNGSTEN ONTO UO_2 POWDER VIA THE WCl_6 PROCESS.

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Introduction: Nuclear Thermal Propulsion (NTP) is under development for deep space exploration. NTP's high specific impulse (> 850 second) enables a large range of destinations, shorter trip durations, and improved reliability. W-60vol%UO_2 CERMET fuel development efforts emphasize fabrication, performance testing and process optimization to meet service life requirements. Fuel elements must be able to survive operation in excess of 2850 K, exposure to flowing hydrogen (H_2), vibration, acoustic, and radiation conditions. CTE mismatch between W and UO_2 result in high thermal stresses and lead to mechanical failure as a result UO_2 reduction by hot hydrogen (H_2) [1]. Improved powder metallurgy fabrication process control and mitigated fuel loss can be attained by coating UO_2 starting powders within a layer of high density tungsten [2]. This paper discusses the advances of a fluidized bed chemical vapor deposition (CVD) system that utilizes the H_2-WCl_6 reduction process.

Problem Statement & Objectives: Crack initiation and propagation is the primary mechanism in an NTP engine by which hot H_2 reduces UO_2 then erodes cermet fuel elements. In addition, if a continuous contact path contact between fuel particles is established rapid and significant UO_2 fuel loss will result [1]. Therefore, in order to minimize fuel loss during operation the fuel particles are coated with layer of high density tungsten. The objective of this development effort is to coat spherical depleted uranium-dioxide (dUO_2) powders with 40 vol% tungsten using the WCl_6 reduction process. Coated powders will not only add defense in layers during operation but prevent powder segregation during can fill, yield a higher green powder packing density, and provide more uniform consolidation during Hot Isostatic Press (HIP).

Apparatus & Procedure: The CVD system is a fluidized bed, raining feed design where the H_2 acts as the fluidization and reaction gas and argon (Ar) acts as a carrier gas, which are regulated to a 10:1 stoichiometric ratio [3]. Approximately 30 g of spherical powder (55-150 μm diameter) is fed into the quartz reactor to achieve a fluidized state. A Pyrex sublimer loaded with 10 g of WCl_6 powder is heated with an electrical heat jacket to between 160-180 °C to sublimate the powder and generate vapor. Ar pushes the WCl_6 reagent vapor from the sublimer to the reactor, which is enclosed in a clamshell furnace heated to 930 °C. These conditions induce the H_2 reduction of WCl_6 reaction as described:

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

Due to the fluidized dUO_2 powder state tungsten will deposit uniformly along surface of each particle. Exhaust gas is run through 0.5 μm filters to retain fine powders, HCl vapor is then removed with an acid trap, and finally excess H_2 is burned by a resistively heated filament exhausted to an overhead fume hood. The W coating thickness is controlled by the sublimer temperature, reactor temperature and duration of reaction. After coating, the powder is maintained in a fluidized state through cool down to remove trace contaminants then removed from system after shut down. Coated powder is transported to an inert glove box for bakeout in a hot H_2 furnace and additional sieving.

Numerous design and process improvements were incorporated into the latest CVD system to include significant design simplification, corrosion resistant materials, active H_2 area monitors, fire detection system, complete enclosure for dUO_2 powder handling, LabView based data acquisition and control system, operator controlled cameras and procedural improvements based on operational experience [4].

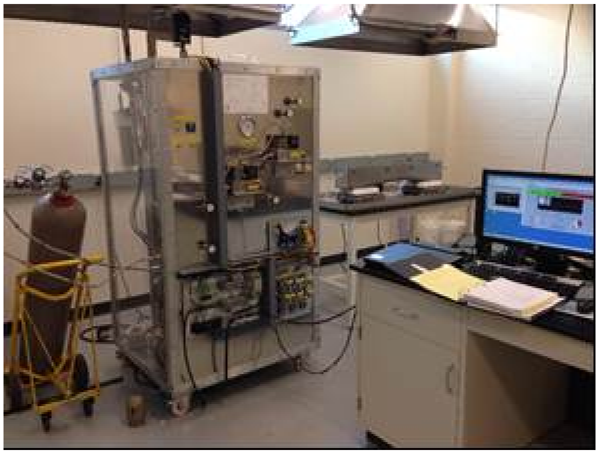

Figure 1. CVD system.

Results: Several coating trials have been completed using surrogate powders and initial results are promising. The increased emphasis on real-time process monitoring and control allows for post-process review of operating parameters that are used to address variation in the deposition results. SEM micrographs show relatively thick W coating are being deposited onto ZrO_2 surrogates powders after only a 20 minute deposition period as seen in Figure 2.

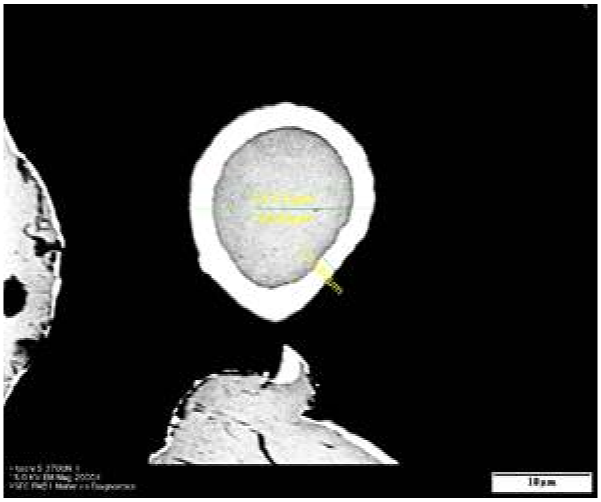

Figure 2. SEM micrographs of tungsten coated ZrO_2 powder at 2,000x.

Coatings on smaller particles appear much thicker when compared to larger particles. Thickness variation as a function of particle size is expected since the rate of deposition is a surface area driven mechanism. Consequently, the best coating results are obtained when a uniform mono-size batch of power is coated. Coatings show relatively good spatial uniformity, no evidence of voids, cracks, or debonding from the substrate. Qualitative EDS spectra results indicate very low quantities of trace impurities as shown in Figure 3.

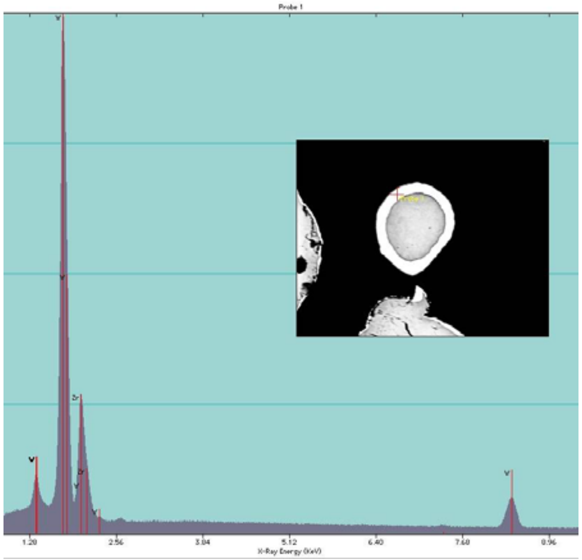

Figure 3. EDS spectrograph of tungsten coated ZrO_2.

Of particular concern is Chloride (Cl) contamination embedded in the deposit as a result of the deposition process. Like previous EDS results, chloride contaminants are on the order of a few percent and those will decrease further by heating the coated powders in an H_2 furnace according to a prescribed schedule. The acceptable limit for specific trace contaminants, such as Cl, within the W coating will require further investigation throughout the fuel development process. Quantitative diagnostic techniques such as electron microprobe will be used to determine quantitative spatial distributions of trace contaminants.

Conclusions: The upgraded CVD system using the WCl_6 process has demonstrated the ability to coat surrogate powders with a dense layer of W. Transition to dUO_2 powder is underway and the initial coating trials are expected to be completed in a few months. Optimization of coating density, adhesion, thickness, and grain boundary orientation will follow. Ultimately, the availability of a dependable supply of W coated UO_2 powder will enable successful fabrication of robust W-UO_2 cermet fuels elements for NTP operation.

Recommendation for Future Work: Subsequent efforts should focus on optimizing process variables to produce repeatable coating batches with desired properties (microstructure, chemical composition, mechanical) to meet service life requirements. Coating runs should use mono-sized spherical powder free of powders outside the nominal size range, particularly fine particles. Quantitative limits for trace contaminants within the coatings must be established in addition to several other quality control measures to ensure an acceptable product will be provided for subsequent fuel fabrication processes. Additional design modifications should be incorporated to provide more forgiving results when off-nominal conditions occur and to provide an additional degree of robustness to allow for faster turn-around between coating runs. In parallel to sub-scale coating efforts the design of an industrial sized CVD system capable of handle kg scale quantities of dU and LEU powder should be investigated in order to facilitate powder coating needs for a full-scale NTP engine development program.

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