Fabrication of High Temperature Cermet Materials for Nuclear Thermal Propulsion

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Abstract

Processing techniques are being developed to fabricate refractory metal and ceramic cermet materials for Nuclear Thermal Propulsion (NTP). Significant advances have been made in the area of high-temperature cermet fuel processing since Rover/NERVA. Cermet materials offer several advantages such as retention of fission products and fuels, thermal shock resistance, hydrogen compatibility, high conductivity, and high strength. Recent NASA funded research has demonstrated the net shape fabrication of W-Re-HfC and other refractory metal and ceramic components that are similar to UN/W-Re cermet fuels. This effort is focused on basic research and characterization to identify the most promising compositions and processing techniques. A particular emphasis is being placed on low cost processes to fabricate near net shape parts of practical size. Several processing methods including Vacuum Plasma Spray (VPS) and conventional PM processes are being evaluated to fabricate material property samples and components. Surrogate W-Re/ZrN cermet fuel materials are being used to develop processing techniques for both coated and uncoated ceramic particles. After process optimization, depleted uranium-based cermets will be fabricated and tested to evaluate mechanical, thermal, and hot H_2 erosion properties. This paper provides details on the current results of the project.

Introduction

The new vision for space exploration has rekindled interest in Nuclear Thermal Propulsion (NTP). Current research by NASA and DOE is focused on resurrecting data from previous programs and initiating development efforts for long lead technologies such as processing of cermet fuel materials. Cermet fuels consist of ceramic particles of uranium nitride (UN) or uranium dioxide (UO_2) dispersed in a refractory metal matrix such as tungsten (W). Typically, the cermet fuels also have an outer refractory metal cladding layer to provide an additional diffusion barrier. The main advantages of the cermet fuel form are retention of fission products, thermal shock resistance, hydrogen compatibility, high thermal conductivity, and high strength. Cermet fuels have been developed and tested on a number of programs such as the GE 710 reactor program and the ANL nuclear rocket program. Significant testing was performed including high temperature in-core, hot hydrogen flow, and thermal shock testing. The results were positive and demonstrated the robust nature of cermet fuels for NTP applications.

Testing during the GE 710 and ANL programs demonstrated the capability of W/UO_2 based cermet fuels to operate at temperatures up to 3000 K in hot hydrogen for several hours. Early in the GE 710 program, W/UO_2 cermet fuels clad with W-25Re were tested for 50 hours in hydrogen at 2860 K and remained leak tight. W/UO_2-ThO_2 cermets clad with W-25Re were also tested at 3270 K for 1 hour, 3170 K for 3 hours, and 3070 K for 10 hours without damage. All tests showed no reaction or sensitivity to flowing hydrogen. The ANL program provided similar results and concluded that W-UO_2 cermet fuels can operate successfully at 3000 K for 50 hours

(Homan 1991). Most of the initial cermet development work was done with UO_2 because of the experience base. However, oxygen migration issues and fuel density limitations led to the consideration of UN as an alternate fuel. Several other matrix and cladding materials were also evaluated including Ta and Mo, but oxygen migration in Ta and the lower melting point of Mo led to the final selection of W-based materials (Anghaie 2004). Also, there was some indication of de-bonding between UO_2 fuel particles and the tungsten matrix during testing at 3000 K, which is likely the result of a thermal expansion mismatch. This could be alleviated by using a W-Re based alloy for the both the matrix and cladding material. It is well documented that small additions of Re improve the strain capability of pure tungsten.

More recent cermet fuel development efforts have focused on UN as an alternative to UO_2. UN fuels have several advantages over UO_2 such as a higher specific uranium content, higher thermal conductivity, lower coefficient of thermal expansion (CTE), and higher operating temperature capability. High uranium content is an important consideration because of difficulties in the processing of high volume percent fuel particle cermets (>50 volume %). A tungsten 72 volume % UN cermet is equivalent to pure UO_2 in terms of uranium loading. The main disadvantage of UN is dissociation into free uranium and nitrogen at high temperatures and the absence of a nitrogen overpressure. However, studies have shown that UN is stable in tungsten at >3000 K as long as the tungsten forms a diffusion barrier to prevent the escape of nitrogen and thus prevent UN decomposition (Takkunen 1969). Ultimately, UN performance could exceed that of UO_2 because of the better CTE match, which reduces cracking and matrix/fuel particle de-bonding from thermal cycling. If cladding failures occur in space, the fuel will gradually vaporize whether it is UN or UO_2. This behavior is well understood for UO_2 but more work is necessary to establish similar data for UN.

Cermet Processing Considerations

Cermets are formed by consolidation or densification of powders using typical Powder Metallurgy (PM) processes such as pressing and sintering, hot pressing, and hot isostatic pressing (HIP). Advanced processing techniques such as Vacuum Plasma Spray (VPS) are also being investigated for the fabrication of multi-layered near net shape parts. Prior to consolidation, the powder materials are blended to provide a uniform distribution of the fuel particles within the matrix. Uniformity is critical for cermet fuel materials because particle clustering can result in localized hot spots and voids. Because of the reactivity of fuel materials such as UN and UO_2, the processing must be performed in a controlled atmosphere. Typically, sintering of W-based cermets is done in a hydrogen atmosphere to help remove carbon and oxygen contaminants. However, sintering in nitrogen or vacuum may be necessary to avoid decomposition of the fuel. Control of the fuel particle stoichiometry is critical because deleterious effects can occur such as the formation of low melting point phases or free uranium. The two main processing routes being pursued on the current program are 1) cold pressing of powders followed by sintering and HIP (without can) to full density and 2) direct HIP of powders using a sacrificial can.

Cold pressing and sintering is the simplest and most well known processing route for producing cermet materials. Various shapes such as plates, disc, rods, and tubes have been fabricated for cermet materials. It has been demonstrated that the densification during sintering of pressed cermet powders is very dependant on the particle size and the sintering time and temperature. Previous work has shown an increase in the sintered density for W/UN cermets fabricated with fine powder particles (Takkunen 1969). Figure 1a shows the effect of finer particle size (increased surface area) of the W and UN powders on the as-sintered density. Decreasing the particle size of the W powder resulted in a slight increase in the as-sintered density. However, a considerably larger increase in the cermet density was achieved by decreasing both the W and UN particle size. The finer particles resulted in finer pores, which require less volume diffusion (and time) in order to consolidate the bulk material.

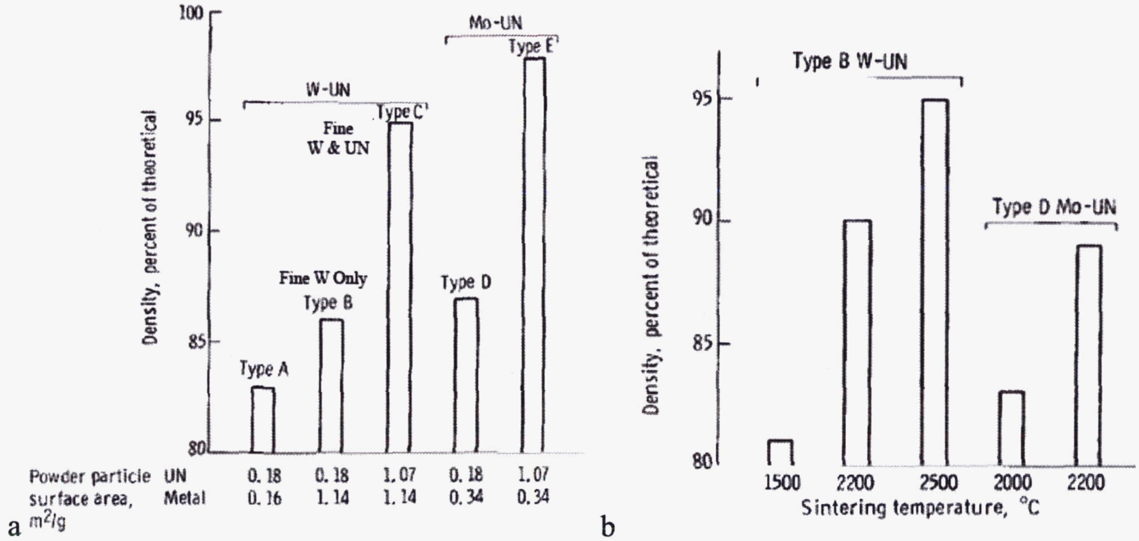


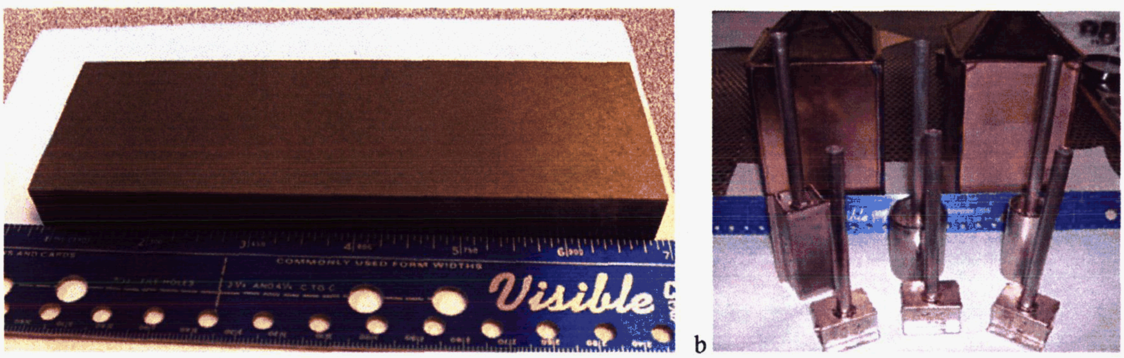
Figure 1: Graphs showing the effect of a) particle size (surface area) and b) sintering temperature on the as-sintered density of W-UN and Mo-UN cermets.

Figure 1b shows the effect of sintering temperature on the density of the W/UN cermets. As expected, increasing the sintering temperature from 1500°C to 2200°C resulted in an increase in density from 81 to 95% of theoretical density for W/UN cermets fabricated with finer particles. Increasing the sintering time had a similar effect of increased density. However, both increased sintering time (in excess of 3 hrs) and temperature were effective in improving the density only when the powder particle sizes were sufficiently small. It should also be noted that sintering of W-based cermet materials results in maximum densities of up to approx 95% for realistic sintering times and temperatures. Typically, sintered parts can be fully consolidated to near 100% theoretical density by hot isostatic pressing (without canning) of the as-sintered part. Hot isostatic pressing techniques that require canning are much more complex.

Direct HIP of cermet powders is also being investigated for the fabrication of cermet fuel materials. The process consist of filling a sealed metal container with the blended cermet powders (or pressed part) followed by full consolidation by HIP. During HIP, the metal can deforms and consolidates the powder at temperatures up to 2000°C and pressures up to 30 ksi. Figure 2a shows images of a HIP'ed W/HfN cermet bar with >99% density. Figure 2b shows various HIP containers used for direct HIP'ing of refractory metals, ceramics, and cermets.

A distinct advantage of sintered cermets is the ability to control the amount of porosity by varying the particle size and sintering conditions. This can be critical because the amount of porosity in a cermet fuel is dependant on the fuel burn-up requirement for the reactor. Reactors with low fuel burn-up, which is the case for relatively short duration NTP applications, can be dense cermets. On the other hand, reactors requiring higher fuel burn-up, such as multi-year power applications, may require a porous cermet fuel to permit fission gas buildup and swelling. There are also disadvantages for the pressing and sintering process route. High density cermets can only be obtained by using fine particle sizes for both the fuel and matrix materials (i.e. W and UN or UO_2). The fine powders pose a significant process handling problem due to the large surface area and reactivity with oxygen. Also, it is not clear whether or not a finer fuel particle (<5 microns) or a coarser fuel particle (5-200 microns) is more beneficial for a nuclear reactor application. Lastly, depending on the reactor application, cermets with fuel loadings exceeding approximately 60 volume percent may be required, which poses significant processing problems for conventional pressing and sintering fabrication techniques.

a



b

Figure 2a: Photograph of HIP'ed HfN/W alloy cermet (> 99% Dense).
Figure 2b: Photo of HIP containers used for HIP'ing of W/HfN billets.
(Photos courtesy of Exothermics, Inc, Amherst, NH)

Current Work

Current work is focused on evaluating fabrication techniques to produce W and W-Re based cermets with 20-60 volume percent UN or UO_2 fuel particles. Conventional PM processing techniques including press/sinter and direct HIP are being optimized to produce single channel tube sections for hot hydrogen testing. A particular emphasis is being placed on low cost processes to fabricate near net shape parts of practical size. Surrogate fuel particles such as ZrN and HfN are being used to evaluate processing parameters such as particle size, composition, fuel loading, initial consolidation techniques, and sintering and HIP conditions. Sintering in both hydrogen and nitrogen is being done to determine the effects on density, fuel stoichiometry, and alloying of the W-Re matrix. Figure 3a shows pressed and sintered W-Re/20 and 40 volume % ZrN disc samples and Figure 3b shows a cold isostatic pressed (CIP) W-Re/60 volume % ZrN rod sample prior to sintering. Similar samples are being fabricated by direct HIP and VPS processes. After optimization, depleted uranium cermets will be fabricated for testing.

Summary and Conclusions

Cermet fuels consisting of UN and UO_2 particles in a W-based matrix are being fabricated for NTP applications. Previous work has demonstrated that W-based UN and UO2 cermets can be fabricated using conventional PM processing techniques. Significant data exist for W-UO_2 cermets from the GE 710 and ANL programs but W-Re/UN cermets have the potential to provide improved performance. Current research is focused on evaluating fabrication processes to produce components for testing in hot hydrogen.

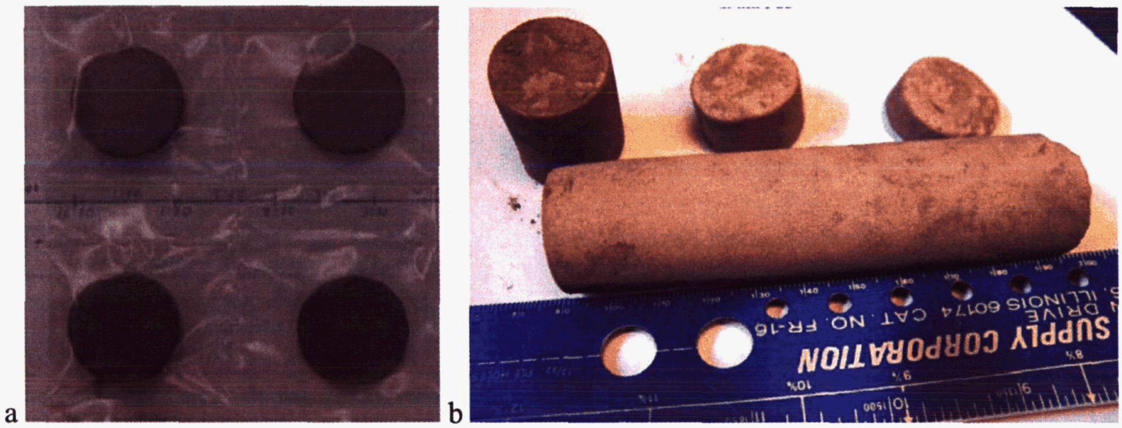


Figure 3: a) Pressed and sintered W-Re/20 and 40 volume % ZrN disc. b) Cold isostatic pressed (CIP) W-Re/60 volume % ZrN rod sample prior to sintering.

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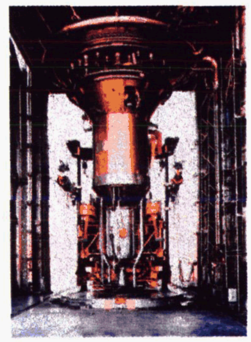

53rd JANNAF Propulsion Meeting
1st Spacecraft Propulsion Subcommittee Meeting
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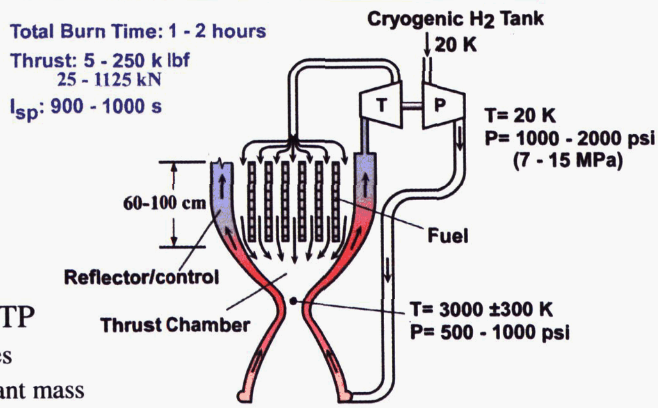
What is Nuclear Thermal Propulsion (NTP)?



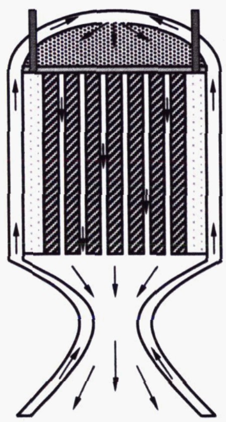
Advantages of NTP

- Shorter Trip times
- Reduced propellant mass
- Increased payload

- Fuels set the upper limit of NTP performance

NTP Fuel Material Requirements

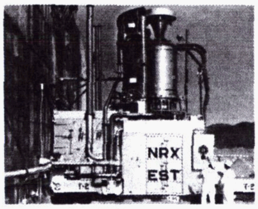
- Very high temperatures 2500-3200K
- 1 hour max single burn
  - Up to 10 cycles
- Hot H2 erosion resistance
- low neutron absorption cross section
- Retain fission products and fuels
- Mechanical strength integrity
- Thermal shock resistance



Previous US NTP Programs

- Rover/NERVA, 1955-1973

  (Nuclear Engine for Rocket Vehicle Applications)
  - 20 rocket/reactors designed, built, and tested
  - Established the feasibility of NTP system
  - Graphite and pure carbide fuels
- GE710 and ANL Programs 1960-1980
  - Developed cermet fuels for NTP
- SNTP, DOD/AF late 1970's-1993
- (Space Nuclear Thermal Propulsion)
  - Developed particle bed reactors (PBR)



NTP Fuel Candidates

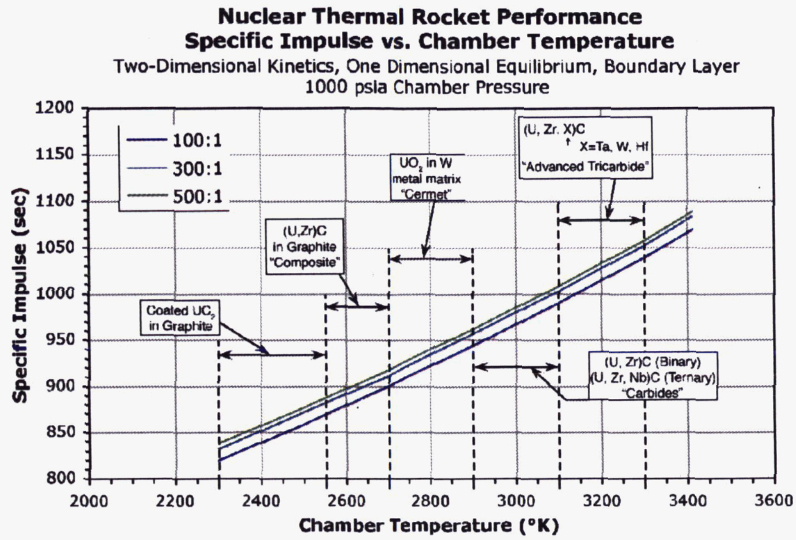
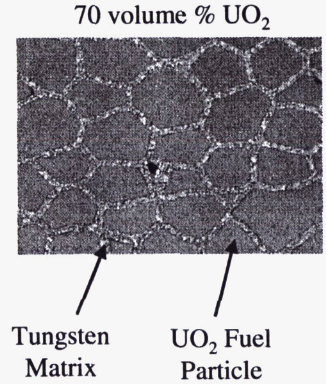


Chart courtesy of Dr. Stan Borowski (NASA GRC)

Cermet Fuel Materials

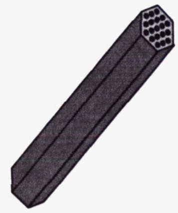
- Refractory metal matrix/dispersed fuel
  - Ceramic fuel particles – UO_2, UN
  - Metallic matrix – W, W-Re, Mo
- Cladding materials – W, W-Re
  - Needed to retain fission products
- Advantages
  - Retention of fission products/fuel
  - Thermal shock resistance
  - H_2 compatible
  - High thermal conductivity
  - High strength

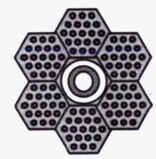
W-UO_2 Cermet
70 volume % UO_2



Cermet Fuel Development

- Cermets developed on several nuclear programs
  - Aircraft Nuclear Propulsion Program (1940's-1962)
  - General Electric 710 Program (1962-1967)
  - ANL Nuclear Rocket Program (1961-1967)
- Over 100 partial and full length fuel test
  - Hundreds of additional samples in support
- 300,000 sample test hours accumulated
  - 12,000 hrs nuclear, >18,000 hrs non-nuclear
  - Thermal cycling up to 2400K, 100 cycles, 100 hours
  - Thermal shock in-core up to 2870K





GE710 & ANL Programs

- GE710 Program
  - Initial work with UO_2
  - O2 migration and fuel stability problems led to UN
  - UN more stable and better CTE match with matrix
- Matrix materials - Ta, W, and Mo alloys
  - Ta - O_2 migration from fuels
  - Mo - low melting point
  - W-based alloys selected for final materials
- Cladding materials – W-25Re, W-Re-Mo alloys
- ANL Program – (similar fabrication techniques as GE710)
  - W/UO_2 with W clad

Demonstrated robust, high performance cermet fuel materials

Current Work at MSFC

Non-Nuclear Materials Fabrication and Evaluation

- Objectives
  - Develop materials and processes for the fabrication of cermets
  - All work to be performed with surrogate and depleted uranium materials
  - Fabricate samples for hot H2 testing
  - Increase experience and capabilities for NTP materials fabrication
- Deliverables
  - Net shape cermet, carbide, and graphite-based hot H2 test elements (PRC)
    - 0.5" diameter x 12" long single channel tubes
  - Processing and characterization data for NTP fuel materials

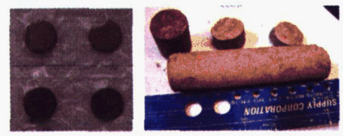
Development Approach

- Start with lessons learned from previous work
  - Rover/NERVA, GE710, ANL, UF/INSPI, Russia
- Materials fabrication development and characterization
  - Investigate forming/joining methods with emphasis on near net shape
  - Characterize compositions, phases, microstructure, etc.
  - Determine chemical compatibility in hot H_2
  - Determine thermodynamics and diffusion phenomena
  - Determine mechanical/physical properties (tensile, CTE, conductivity)
- Optimize processing and fabricate test samples
- Subscale Non-nuclear hot H_2 testing
  - Laboratory furnace (static), Arc Jet (flowing)
  - Lifetime, cyclic
- Non-Nuclear testing of prototypical single elements (MSFC PRL)
  Nuclear Thermal Rocket Element Environmental Simulator (NTREES)

Current Work at MSFC

W, W-Re/UN and UO2 based cermets

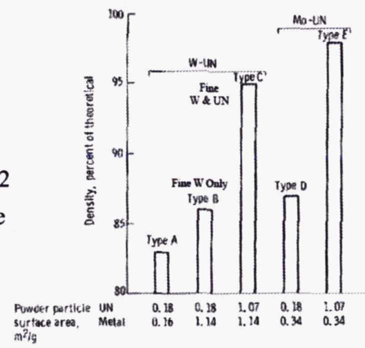
- Investigate conventional PM processing such as CIP, sintering, and HIP
  - Near net shape tubes, rods, discs
  - ZrN or HfN surrogate materials



Press/Sintered W-Re/ZrN 20, 40, 60 vol% Cermets

Press/sinter (with HIP to full density)

- Sintered density very dependant on powder characteristics
- Axial pressing of test samples
  - Sintering time, temp, atmosphere (H2, N2
  - Powder size, morphology, purity, particle loading (20-60 volume %)
- CIP of larger rod and net shape tube



Current Work at MSFC

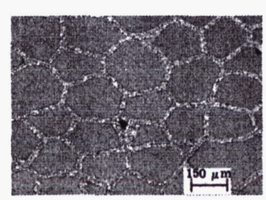
Direct HIP

- Powder materials canned and evacuated prior to hot isostatic pressing
- Rods, net shape tubes
- Not as sensitive to powder characteristics

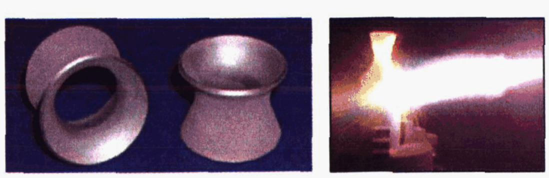
Misc. HIP Cans

Vacuum Plasma Spray (VPS)

- Tubes with integral W-Re clad
- Surrogates only



HIP'ed W/UO_2



Vacuum Plasma Sprayed W and W-Re Nozzles

Current Progress at MSFC

- Depleted uranium license is being pursued with NRC
  - Approval expected early in CY06
- M&P foundry is being converted into a controlled access area for processing of dU materials
  - High temperature graphite furnace (3000C) is being fabricated
  - 2 inert glove boxes are being installed
  - Large work table with vent hood and limited access points
  - PM processing equipment (press, dies, blending, sieving, milling, etc.)
  - Dedicated metallography equipment (diamond saw, grind/polisher)
- Cermet processing trials using surrogates
  - 1st iteration press/sinter complete, 2nd iteration trials in progress
  - VPS (Contractor) and direct HIP (In-House) trials to begin 12/05

Summary

- Renewed interest in NTP to support space exploration
- NTP systems offer higher Isp
  - Shorter trip times
  - Reduced propellant mass and increased payload
- Fuel materials set the limit of NTP performance
  - Higher temperature fuels provide more Isp
- Cermets have been demonstrated for NTP applications
  - Excellent retention of fission products
  - High strength and conductivity
  - Very tolerant to nuclear excursions
- Cermets materials and processes are currently being developed at MSFC to support non-nuclear testing
  - Conventional PM processing with emphasis on near net shape
  - Properties very dependant on powder characteristics and processing
- Developing W-based cermets with UN and UO2 fuel particles