INVESTIGATION OF PRODUCTION PARAMETER EFFECTS ON SPARK PLASMA SINTERED MOLYBDENUM CERMET WAFERS FOR NUCLEAR THERMAL PROPULSION APPLICATIONS

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This study focused on nuclear fuel fabrication using powder blending and spark plasma sintering (SPS) of Mo-ZrO_2 surrogate ceramic-metal (cermet) fuels. The study consisted of two co-projects: a powder blending/distribution study and an SPS parameter optimization study. The powder blending study focused on optimization of the powder processing parameters in order to fabricate high density cermets with uniformly distributed ceramic microstructures. The SPS parameter optimization study focused on the impact of sintering parameters (temperature, dwell time, and pressure) on the microstructural properties of a cermet (density/porosity, grain structure, and hardness). In the powder blending and distribution study, addition of 0.1 wt% and 0.5 wt% binder resulted in complete coverage and even distribution of large, spherical ZrO_2 particles with Mo powder for batches of 50 vol% and 60 vol% ceramic loading respectively. When optimizing SPS parameters, fuel density (decreased porosity) was directly related to increase in sintering temperature, pressure, and time. Optimal sintering parameters suggested from this study, for Mo-ZrO_2 cermet wafers with 60 vol% ceramic loading, were found to be at a temperature of 1400ºC, at 50 MPa uniaxial pressure, for at least 5 minutes dwell time.

I.   INTRODUCTION

Nuclear thermal propulsion (NTP) is based upon the principle of heating a low mass propellant, such as hydrogen (H_2), via the heat from fission and expanding it through a nozzle to produce high in-space thrust (15,000 - 250,000 lbf) and specific impulse (750 - 1100 s). NTP is actively being researched by NASA and other private, university, and government partners to enable fast transit times for missions beyond low Earth orbit (LEO). Several methods enabling this form of propulsion are under scrutiny, including the use of ceramic-metal (cermet) fuel systems. In cermet fuel systems, ceramic fissile fuel particles (such as UO_2, UN) are encapsulated by a metal matrix that is composed of an inert refractory metal, such as tungsten (W) or molybdenum (Mo). Cermet fuel wafers are currently being manufactured via spark plasma

sintering (SPS) techniques, which consolidates blended cermet powders into a net-shape fuel pellet. In this process, sintering is facilitated by passing a DC current through a graphite die to heat sample powders to very high temperatures, while applying uniaxial force. This study explores the optimal cermet wafer production methodology for Mo-matrix cermets using ZrO_2 microspheres as a surrogate for UO_2. Originally developed by Tucker et al. for W-matrix cermets, a two-step powder blending/SPS sintering process was utilized to optimize the fabrication of cermets with desirable microstructures.[3]
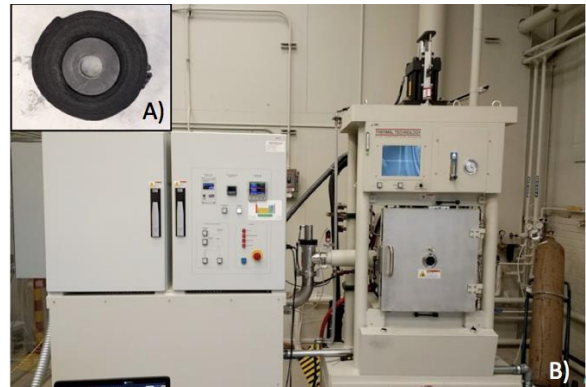
Fig. 1. The SPS machine presses blended cermet powder into a dense pellet at high temperatures with uniaxial force. The powder is inserted into a die (A) which is placed in the SPS furnace (B).

## II.   PRE-SINTERING POWDER BLENDING PROCESS OPTIMIZATION

Prior to sintering, Mo and ZrO_2 powders are blended with a polyethylene binder to create a uniform distribution of ceramic fuel particles within the metal matrix. In this study, the powder blending process was evaluated to identify the impact of binder addition on uniformity of powder coatings of as blended mixtures and particle distribution of as-fabricated cermet microstructures, for variable fuel volume loadings (50, 60 vol% ceramic). It is desired that the cermet microstructure allows for uniform particle distributions which eliminate interconnectivity of

the ceramic phase. Powder blending is performed via addition of a polyethylene binder to the initial powders, powder mixing, and blending via heating of the binder above the binder drop point to allow for adherence of metal powders to ceramic microspheres. Binder is then burned off from the cermet mixture during sintering.

II.A. Experimental

Spherical ceramic ZrO_2 particles (~250 µm diameter) and metal Mo powders (~5 µm) are measured on an analytical balance to attain the desired volume ratio of metal to ceramic. A polyethylene binder addition (or lack thereof) was measured and added to each batch in quantities spanning between 0 – 1.00 wt%. The mixtures were transferred to a Turbula® shaker mixer and shaken for approximately one hour. At this point, the mixed powders appear homogeneous, so that there was no obvious localized separation of the larger ZrO_2 particles from the finer metal powders/binder via visual inspection. Mixtures containing binder addition are transferred into a beaker, heated on a hotplate above the binder drop point (170 – 185 °C), and stirred with a stir bar (revolving at 100 - 200 rpm) for approximately 10 minutes until the powder mixture appeared homogeneous. Heating and stirring is terminated once all white ZrO_2 spheres are fully coated (unobservable without a visual aid) and the mixture had begun to agglomerate. Blended powders were inspected using scanning electron microscopy (SEM) to characterize metal powder coating uniformity.

In order to analyze the effectiveness of the powder blending process on the fabrication of cermet wafers with ideal microstructures, a study analyzing the distribution of ZrO_2 throughout the Mo-matrix was performed. Blended powders of 50 and 60 vol% cermets with and without binder addition were fabricated using SPS. For each mixture, ~13 g of powder was transferred into a 20 mm diameter Grafoil® lined graphite die and sintered in a Thermal Technologies DCS-15 SPS furnace using the sintering parameters (sintering temperature, pressure and dwell time) of 1500 °C, 5 minutes, 50 MPa. The produced cermet wafers were ground flat using silicon carbide (SiC) paper until the surrounding Grafoil® is removed. Ground samples were cross sectioned using a diamond saw and mounted in epoxy for polishing and microstructural characterization of the radial and axial variation in particle distribution (fig. 2). The samples were mechanically polished using SiC paper to a 4000 grit (5 µm particles) finish and axial and radial ceramic distributions observed using optical microscopy (OM).
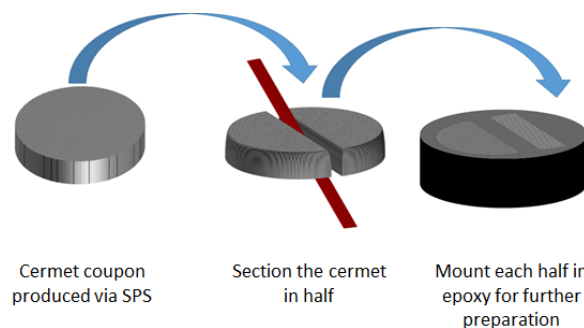

Fig. 2. Cermet coupon preparation method after SPS. The sample is then polished to a mirror finish and analyzed via optical microscopy for a uniform particle distribution.

II.B. Results

II.B.1. Powder Blending Optimization

When optimizing the powder blending process, it is desired to determine the required addition of binder to allow for uniform particle coatings, while minimizing powder clumping. Blended mixtures with varying binder additions were inspected using SEM to determine which binder addition yielded the most uniform complete coverage of metal coatings on ceramic fuel particles (fig. 3). Within 60 vol% cermets experimented on previously, maximum ZrO_2 coating was observed with 0.5 wt% binder addition. Addition of this much binder to 50 vol% cermets resulted in self-adherence of the Mo (fig. 3-E & F). Reduction to 0.1 wt% binder resulted in adequate coating for 50vol% cermets. (fig. 3-C).
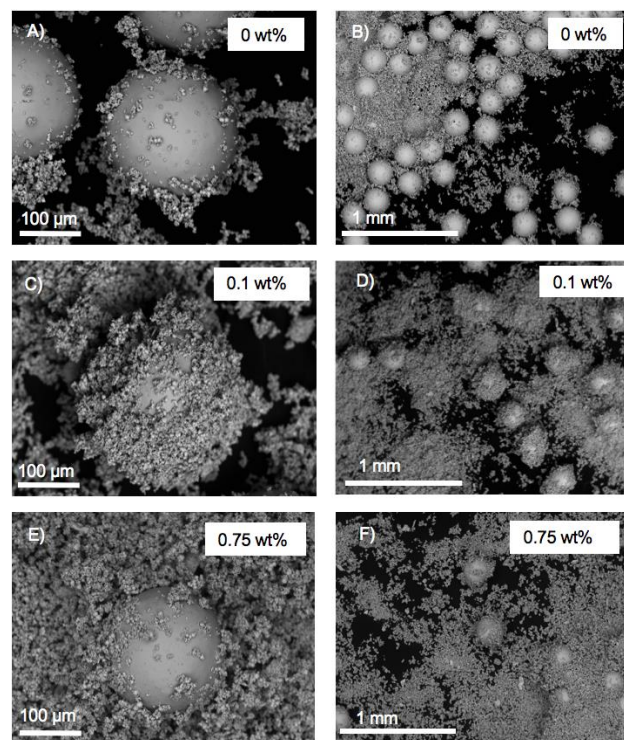
Fig. 3. An optimal amount of binder for the 50 vol% Mo-cermet is 0.1 wt% (C & D). The ZrO_2 particle is well covered in Mo (C & D) and the particles are evenly spaced allowing for a full ZrO_2-Mo coverage (D). A greater or lesser wt% of binder creates a lack of ceramic coverage and an uneven particle distribution.

II.B.2. Particle Distribution Study

Upon analysis of radial and axial optical micrographs taken of the cross sectioned samples, ZrO_2 distribution was found to be much more uniform with addition of 0.5 wt% binder in 60 vol% cermets, and 0.1wt% binder addition within 50 vol% cermets.

Fig. 4 below is a visual representation of two cermets of the same composition prepared through blended powders (Fig. 4-A, B) and without blending (Fig. 4-C, D). The powder blending process produces a more homogenous 60 vol% sample and prevents ceramic and metal segregation during loading of powders prior to sintering. Incorporation of the powder blending process in cermet fabrication is necessary for optimized microstructures for high volume loading cermets (>50 vol%).
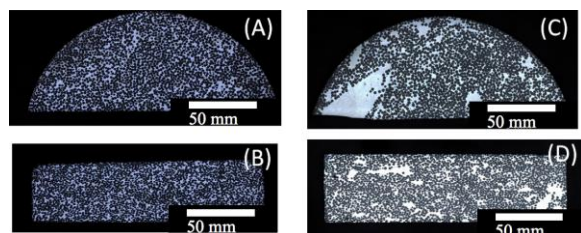
Fig. 4. (A) & (B) show distribution of ZrO_2 in a 60 vol% cermet with 0.5 wt% binder addition. (C) & (D) show distribution without addition of binder.

III.   SPS PARAMETER OPTIMIZATION

To identify the optimal sintering parameters for Mo-matrix cermets using SPS, three variables were studied: dwell time, temperature, and pressure. Dwell times of 5 - 30 minutes and sintering temperatures of 1100 – 1400 °C were considered. A standard applied pressure for Mo-cermets was chosen as 50 MPa and was held constant until the variables of dwell time and temperature are optimized. Once optimized temperature and dwell time parameters were established, sintering pressure was varied (5, 10, 25, 50 MPa). After sintering, the as fabricated Mo-cermet microstructure was characterized to understand impact of sintering parameters on cermet density, matrix density, and particle-matrix bonding.

III.A. Experimental

A standardized blended powder mixture of 60 vol% Mo-ZrO_2 (0.5 wt% binder additions) was utilized for optimization of SPS parameters. For each sample, 13 g of blended powder was loaded into a 20 mm diameter Grafoil® lined graphite die and sintered at temperatures of 1100, 1200, 1300, 1400, and 1500 °C for 5 minutes. These dwell times and temperatures were chosen for initial study due to diminishing return (or a reduced increase in density) anticipated during the sintering process. This behavioral trend has been seen previously for W-CeO_2 cermets[3] in addition to this project. Throughout the entirety of the study, ramp rate was held constant with: 100 °C/minute and 10 MPa/min to maximum temperature and pressure.

After sintering, fabricated cermets were ground flat using SiC paper until the Grafoil® layer was removed from all faces of the sample. Once this sacrificial layer was removed, samples were weighed and as fabricated cermet density was determined via the Archimedes method. A Sartorius Practum 224-1S analytical balance was used to obtain room temperature weights of each cermet sample in air and in deionized (DI) water. Once weighed, samples were prepared for microstructural analysis using OM and SEM. Samples were polished to a 1μm finish using a Struers LaboForce-100 auto polisher. The polishing process required the following SiC paper polishing, followed by diamond suspension polish to complete the mirror finish varying from 15-25 N force: 80 grit (ground until flat), 180 grit (4 mins), 320 grit (4 mins), 500 grit (4 mins), 600 grit (4 mins), 800 grit (4 mins), 1200 grit (4 mins), 2000 grit (4 mins), 4000 grit (4 mins), 9μm suspension, 3μm suspension, 1μm suspension.

III.B. Results

Using Archimedes principle, the density of cermet samples was calculated and compared to the theoretical density (TD) of an ideal 60-vol% Mo-cermet (7.80 g/cm^3), as shown below in Table I. The SPS parameters each correspond to its cermet density, and an optimal density of 7.57 g/cm^2 (97.46%) is chosen. Even though a greater dwell time and temperature proved a greater density than the chosen optimal, the selected has a lesser dwell time and therefore requires less power and funds to fabricate.

Overall, cermet density did correlate with increasing pressure for high applied pressures 25 - 50 MPa (Table II), however porosity was observed to be relatively independent of sintering pressure at low pressures (< 25 MPa). Minimal density improvements were seen when varying pressure between 5, 10, and 25 MPa, however a large shift in cermet density was observed for 25 and 50 MPa applied pressures. For application in production scale processing of Mo-cermet wafers, when optimizing the sintering process, applied pressures should not result in great benefit to the overall wafer density if sintering at low pressures (5 - 25 MPa).

Polished samples were inspected via SEM to analyze the effects of applied sintering pressure on sample microstructure and porosity (fig. 5). In this study, sample

porosity was found to increase with reduced sintering temperature, dwell time, and applied pressure. Porosity, especially interconnected porosity, acts as an easy pathway for H_2 ingress into the pellets, thereby leaving the ceramic fuel particles more susceptible to hydrogen attack during operation. Fig. 5-A,B,D show low levels of porosity formed when sintering at 1400 °C at varying dwell times and pressures. Fig. 5-C demonstrates a representative microstructure formed at the low temperature extreme where porosity is more prevalent in the metal matrix and a large void space is also present due to poor sintering of the metal matrix.

Fig. 6 demonstrates representative microstructures of cermets with desirable and undesirable ceramic-metal matrix interfaces. It is desirable for the metal matrix to have both low porosity and the microstructure to sustain a diffusional bond of the metal matrix with the ceramic fuel particles. Fig. 6-A exhibits a cermet microstructure with diffusional bonding of the ceramic and metal phases, the perimeter of the ceramic is surrounded completely by the Mo-matrix and diffusion of the Mo/ZrO_2 over the entirety of the interface occurs. In fig. 6-B, the ceramic particle is surrounded by the metal matrix, however no diffusion occurs, therefore particles are held much more loosely within the metal matrix and are more susceptible to pullout during preparation or fallout during handling.

A diffusion bonded interface is observed in the optimally sintered cermets and is anticipated to result in more desirable thermomechanical properties of the fuel and better fuel performance. Relatively low porosity was seen in the metal matrix for all samples, but more pores, void areas (caused by pullout of ZrO_2 particles during sample preparation), and poor interfacial bonding at the metal cermet interface (fig. 6-B) were seen in the microstructure of cermets sintered at 1100 °C (fig. 6-B, fig. 5-C). The optimally sintered samples in the upper temperature and time ranges showed not only a lack of macro-cracks and void space, but also optimal interfacial bonding (fig. 6-A) and overall higher %TD for these samples (fig. 6-A, fig. 5A,B,D).

TABLE I. Dependence of as produced cermet wafer density and %TD with respect to sintering dwell time and temperature, fabricated with 50 MPa applied pressure

Density (%TD) (g/cm³)	Sintering Temperature (°C)				
	1100	1200	1300	1400	1500
Dwell time (min) 5	90.74 (7.080)	95.06 (7.407)	95.26 (7.494)	**97.46** (7.573)	96.72 (7.536)
10		95.74 (7.451)	97.63 (7.569)	97.97 (7.606)	98.1 (7.612)
30		95.90 (7.452)	97.97 (7.612)	98.57 (7.612)	

TABLE II. SPS Pressure Analysis: 1400 °C for 5 minutes Raw Density and %TD

Pressure (MPa)	Density (g/cm³ | %TD)
5	7.422 | 95.68
10	7.423 | 95.69
25	7.427 | 95.79
50	**7.573 | 97.46**
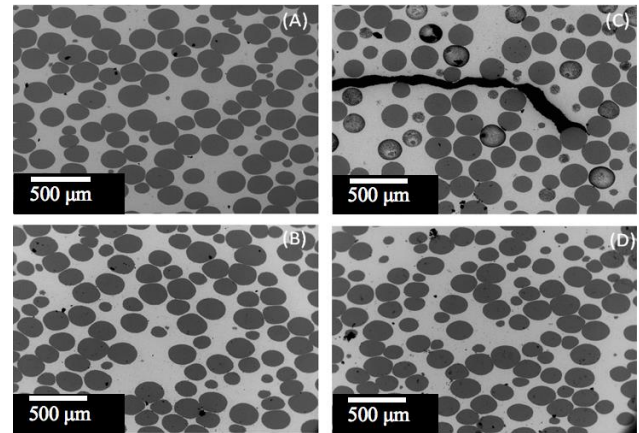
Fig. 5. Back scattered electron image of Mo cermets produced with varying sintering temperatures, pressures, and dwell times: (A) 1400°C-5 minutes-50 MPa (optimal), 7.753 g/cm³ (B) 1400 °C-5 minutes-5 MPa, 7.422 g/cm³ (C) 1100 °C-5 minutes -50 MPa, 7.080 g/cm³ (D) 1400 °C-30 minutes-50 MPa, 7.612 g/cm³.
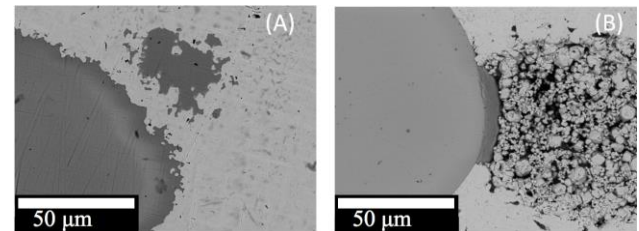
Fig. 6. Difference between a strong (A) and weak (B) interfacial bond of the ceramic particle and metallic matrix for cermets sintered at (A) 1400°C for 5 minutes at 5 MPa and (B) 1100°C for 5 minutes at 50 MPa.

IV. CONCLUSIONS

In this study, the impact of powder preparation and sintering parameters on "as fabricated" Mo-cermet wafer

microstructure was explored using ZrO_2 as a surrogate for UO_2. The criteria for an optimized cermet microstructure in this study consisted of:

- Fully dense and sintered metallic matrix (low porosity).
- Diffusional interfacial bonding of the metal matrix and ceramic fuel particles.
- Uniform ZrO_2 distribution throughout a Mo-matrix without agglomeration (minimal interconnectivity) of the ceramic particles.

In this study, the applications and intricacies of the powder blending process, previously demonstrated for the fabrication of W-UO_2 cermet wafers, were explored for the fabrication of Mo-cermets with desirable microstructures. It was found that optimal binder addition is dependent on ceramic volume loading and lower ceramic volume loadings (< 60 vol%) required less binder addition than high fuel volume loading cermets. As-sintered wafer fuel distribution was independent of the powder blending distribution for low volume loadings (40, 50 vol%). When excessive binder was added to the mixture, metal powders were observed to agglomerate resulting in more segregated sintered microstructures. However, for 60 and 70 vol% fuel loadings, much more desirable microstructures were fabricated using blended powders (with optimal binder coating) rather than the as mixed powders.

As a second part to this study, the impact of SPS parameters on 60 vol% loading cermet microstructures were explored. Processed cermets were formed into near TD compacts consisting of a metal matrix with closed porosity and with a diffusion bonded interface to the fuel surrogate particles at sintering temperatures exceeding 1200 °C. Density was found to increase, and porosity decreased with increasing process temperature and dwell time, with >97% TD achieved at 1400 °C, 5 minutes, 50 MPa pressure. Processed cermet density was relatively independent of pressure in the low-pressure range (5 - 25 MPa). A large shift in cermet density was observed for 50 MPa applied pressures (> 97 %TD) compared to low pressure (~95 %TD). The optimized sintering parameters (1400 °C, 5 min., 50 MPa) suggested in this study that high TD in wafer fabrication corresponds to a high sintering pressure (50 MPa). If very high cermet densities (>97 %TD) and low processing pressures (< 25 MPa) are desired, it is suggested future optimization studies focus on increased sintering temperatures or dwell times.

ACKNOWLEDGMENTS

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