A Methodology for Producing Uniform Distribution of UO_2 in a Tungsten Matrix

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Abstract: We report a method to produce a uniform mixture of uranium dioxide spherical particles in a tungsten matrix. This method involves mixing 0.5 weight percent of high density polyethylene binder with 60 volume percent uranium dioxide spheres and 40 volume percent tungsten powders. Initially, hafnium oxide spheres were used as a surrogate for uranium dioxide spheres. The $\text{HfO}_2/\text{W}/\text{PE}$ powders were thoroughly mixed in a Turbula, then mixed on a hot plate above the drop point of the binder. These powders were then densified using spark plasma sintering. Microstructure was evaluated using scanning electron microscopy, density was measured and hardness measurements were made. Initial carbon content of the powders were measured and carbon content of the sintered materials was measured. Subsequently, $\text{W}/\text{UO}_2/\text{Binder}$ powders were mixed using the same methodology to ensure the process could be used for this system. These powders were sintered using hot isostatic pressing and microstructures evaluated. The resultant microstructures contained uniform distribution of HfO_2 and UO_2 particles in the tungsten matrix with very low carbon content.

Key words: Nuclear propulsion, tungsten, depleted uranium oxide, hafnium oxide, powder processing, spark plasma sintering.

1. Introduction

Many believe that NTP (Nuclear thermal propulsion) is the best near term option for crew and cargo missions to the Moon, near earth objects, Mars and other deep space destinations. The belief is due to increased performance and reduced trip times as compared to current chemical rockets. The feasibility of NTP was established in the 1960's during the joint NASA (National Aeronautics and Space Administration) and Atomic Energy Commission Rover/NERVA (Nuclear engine for rocket vehicle application) Program [1]. However, many questions on the nuclear fuel performance and affordability still remain. A key enabling technology for future NTP systems is the fabrication of a stable high temperature nuclear fuel form that can operate at temperatures up to 2,500 °C. The fuel materials need to be chemically compatible with the coolant/propellant, typically hydrogen, and able to withstand stresses introduced from thermal

gradients [2]. The focus of this paper is on cermet fuels composed of ceramic fuel particles embedded in a refractory metal matrix. Considerable research was done at NASA and DOE (Department of Energy) laboratories to characterize the behavior of tungsten uranium dioxide (W/UO_2) fuels at high temperatures [3, 4]. The primary failure mechanisms is the loss of structural integrity due to the high vaporization rate and decomposition of UO_2 at temperatures above 2,000 °C. The failure mechanisms and materials and processes used to minimize fuel loss are well defined in open literature [5].

Various methods for consolidation of W/UO_2 fuel elements have been evaluated including hot isostatic pressing, hot pneumatic impaction, and traditional green pressing and sintering. Most of the initial W/UO_2 Cermet development was done with blending of fine angular W and UO_2 powders [6]. Subscale test samples made from the powder mixtures were performed reasonably well, but suffered from significant fuel loss during repeated thermal cycling due to agglomeration of the non-symmetric UO_2 powders. The blended

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powder mixtures resulted in a non-uniform dispersion of the UO_2 particles in the tungsten matrix, which allows rapid vaporization of the interconnected UO_2 from the sample edges into the bulk material. Also, the non-symmetric powders create areas of stress concentrations due to thermal expansion mismatch, which eventually crack the tungsten matrix. Evenly coating spherical UO_2 particles with CVD tungsten prior to consolidation was demonstrated to provide improved performance. Conclusions from the research stated that it is critical to stabilize the fuel particles and protect them within a uniform matrix of tungsten. However, the CVD processes demonstrated in the 1960's do not currently exist and there are technical issues with impurities and long reactions times necessary to apply the appropriate thickness coatings.

Binder assisted processing techniques are widely used in the fabrication of ceramic and metal components [7]. It is extremely important to produce homogeneous mixtures of particles of not only different materials but also materials of different sizes. An example is powder injection molding where the end product is a result of a compound of thermoplastic polymer and powder in which the binder is removed upon sintering. The powder/binder mixture is an important phase in the process, since the uniformity of mixture influences flow behavior of the feedstock and sintered properties [8]. The presence of agglomerates alters the flow behavior of the feedstock and can cause defects in the sintered body [9-12].

The properties which give rise to segregation in powder mixes are different in particles size, density, shape and particle resilience [13]. However, difference in particle size has been shown to be the most important of these effects [13]. Particle segregation causes fluctuations in the size distributions of particles and this in turn leads to variations in bulk density which can further effect the desired properties [13]. There are three mechanisms of segregation which can occur during mixing and vibration. Trajectory segregation can occur during mixing whereby fine

particles travel further than coarse particles during the mixing operation [13]. If a mass of particles is disturbed such that individual particles move, a rearrangement takes place via percolation. Over time gaps between particles can occur, allowing a particle from above to fall down, while a particle from some other location replaces it. If the powder mass contains particles of different sizes, it will be easier for a small particle to fall through the larger particle interstices leading to segregation [13]. This percolation can occur when the mass of particles is disturbed due to a shear stress within the powder mass, due to pouring, stirring, shaking and vibration [13]. Coarse particles can rise during vibration leading to another mechanism of segregation. The explanation for this phenomena is that a large particle causes an increase in pressure in the region below it which compacts the material and stops the particle from moving downward. Any upward movements allow fines to run in under the coarse particle and these in turn are locked in position. If the intensity of the vibration is suitable, the large particle will move to the powder surface [13].

The use of binders in cermet systems can overcome some the above mention segregation problems. Typically, one can use a solvent based binder for low temperature processes or a plastic binder for higher temperature applications. In most processes up to 35 weight percent, binder is used to insure good flow characteristics [14]. On binder burnout this can lead to large amounts of residual carbon left in the final part. For nuclear thermal propulsion fuels, carbon amounts above parts per million is to be avoided due to carbon reaction with hydrogen which can lead to internal pressures and cracking of the fuel element.

The purpose of this study was to devise a simple and inexpensive method to produce uniform mixtures of spherical particles in a tungsten matrix containing low carbon content.

2. Materials and Methods

Tungsten powders, H. C. Starck 15/5 μm , were used

for the matrix material. Spherical HfO₂ particles (~250 µm diameter) were made via an alginate process and provided by Oak Ridge National Laboratory. Spherical UO₂ particles were produced by sol-gel process and provided by Oak Ridge National Laboratory. Honeywell provided 8 different types of possible binders for the process. These binders are shown in Table 1 below including Mettler drop point, viscosity at 140 °C and density.

The A-C 617 and A-C 617A have identical properties as can be seen from the table, the only difference being the starting particle size for the A-C 617 was larger.

Initially, the binder was milled using alumina balls in a Turbula for 30 min to decrease the initial polymer particle size. Next, tungsten, HfO₂ and binder were mixed for 30 minutes in a Turbula in order to disperse the binder uniformly within the powder. Binder amounts were 0.25, 0.5 and 1.0 wt.%. The powder was then stirred on a hot plate/magnetic stirrer at 5 °C above the drop point for 5 min. The powders were then examined using scanning electron microscopy to determine if the smaller tungsten particles adhered to the larger HfO₂ particles. Based upon this examination, a final binder was selected for use in consolidating the powders into a uniform, dense microstructure. Binder weight percent's tested were 0.25, 0.5 and 1.0. SPS (Spark plasma sintering) was performed at ORNL (Oak Ridge National Laboratory) to densify the samples. SPS utilizes pulsed current directly through the sample which results in densification in much less time and lower temperatures than traditional sintering

techniques. The total 8 samples were sintered in the SPS at temperatures of 1,400, 1,500, 1,600 and 1,700 °C for 20 min and uniaxial pressure of 50 MPa. Carbon content of starting powders and densified samples were performed using instrumental gas analysis. Density of the sintered samples was performed using the Archimedes method. The samples were then cut in half using a diamond wafering saw and mounted in epoxy for grinding and polishing according to the schedule below:

- (1) 70 µm coarse SiC, water lubricant until graphoil removed;
- (2) 240 grit coarse SiC, water lubricant 5 min;
- (3) 400 grit coarse SiC, water lubricant, 5 min;
- (4) 600 grit coarse SiC, water lubricant, 5 min;
- (5) 800 grit coarse SiC, water lubricant, 5 min;
- (6) 9 µm fine diamond, glycerol lubricant, 6 min;
- (7) 3 µm fine diamond, glycerol lubricant, 6 min.

Samples were then examined using scanning electron microscopy to determine microstructure and energy dispersive X-ray analysis was performed to determine chemical distributions. Hardness was determined using Vicker's Microhardness indentation with 0.5, 1.0 and 2.0 kg loads being used. Five indents were made at each load level.

W/UO₂/Binder powders were produced in the same manner as the W/HfO₂/Binder powders. We were unable to sinter these samples with SPS at ORNL due to their lack of a nuclear license for this instrument. We therefore used the hot isostatic press at Marshall Space Flight Center to densify the samples. First, a 0.25 diameter tube was filled with the W/UO₂/Binder

Table 1 Polymer types tested as binders with properties.

Trade name	Polymer	Density (g/cc)	Drop point (°C)	Viscosity at 140 °C (cP)
A-C 1702	Polyethylene homopolymer	0.88	90	30
A-C D-12	Polyethylene homopolymer	0.94	118	-
A-C B-12	Polyethylene homopolymer	0.96	126	-
A-C 617	Polyethylene homopolymer	0.91	101	180
A-C 617A	Polyethylene homopolymer	0.91	101	180
A-C 575A	Ethylene maleic anhydride copolymer	0.92	106	4,200
A-C 400A	Ethylene vinyl acetate copolymer	0.92	92	595
A-C 540A	Ethylene acrylic acid copolymer	0.93	105	575

powder. The tube was then heated for 1 h at 300 °C, ramped to 500 °C and held for 1 h in vacuum. The starting vacuum was 6×10^{-6} Torr, 5×10^{-3} Torr during heating and was 3×10^{-4} Torr upon cooling down to room temperature. The sample was then hot isostatic pressed at 1,800 °C, 27,000 psi for 4 h. Sections were cut and polished for scanning electron microscopy examination.

3. Results and Discussion

It was observed from scanning electron micrographs the degree to which each binder was able to adhere tungsten particles to the larger HfO_2 spheres. It was found initially that the 0.5 wt.% binder worked the best. When 0.25 wt.% binder was used almost no coverage of the HfO_2 , particles with tungsten occurred. When 1.0 wt. % was used, clumping of the tungsten particles occurred. Fig. 1 of the HfO_2 particles with tungsten occurs, most of the tungsten is clumped together between the HfO_2 particles. The viscosity of this polymer at 140 °C is 595 cP, which is one of the highest viscosity shown in Table I.

Fig. 2 is the result when the binder is EAA (Ethylene acrylic acid). As one can see from this figure the coverage of tungsten particles on the HfO_2 particles is much better. Here the viscosity (Table 1) is lower than that for the EVA (Ethylene vinyl acetate) copolymer shown in Fig. 1.

The most satisfactory results were obtained for the PE (Polyethylene) homopolymer, as A-C 617A shown in Fig. 3.

As one can see from (Fig. 3), the HfO_2 particles are completely coated with very little tungsten left between the HfO_2 particles. This binder has a viscosity at 140 °C of 180 cP. Thus at 10 °C above the drop point for this material, the polymer viscosity should be such that it can easily coat the HfO_2 particles allowing the smaller tungsten particles to adhere. It is likely that the mechanism of bonding between the polymer and tungsten and polymer and HfO_2 is van der Waals bonding. All of the other binders tested had poorer

coverage than the A-C 617A. The A-C 617 was not as good, but this was due to the much larger starting particle size, millimeter sized versus micron size particles. To test this, the A-C 617 polyethylene was ball milled for 1 h in order to reduce the particle size.

Fig. 1 W/ HfO_2 /EVA Binder Powder Mixture.

Fig. 2 W/ HfO_2 /EAA Binder Powder Mixture.

Fig. 3 W/ HfO_2 /617A PE Binder Powder Mixture.

In this case the coverage of HfO₂ particles with tungsten particles was similar to that shown in Fig. 3 for the A-C 617A. In the cases shown in Figs. 2 and 3, one can imagine the large spherical HfO₂ particles rolling around the bottom of the beaker during stirring under heat and picking up the smaller tungsten particles resulting in the images shown in these figures.

The Archimedes method was used to determine percent of theoretical density for the SPS sintered samples. These samples used the A-C 617A polyethylene binder. The results are shown in Table 2.

The first two runs were at 1,400 °C and 1,500 °C for 5 min. The low densities resulted in the sintering time being increased to 20 min. One can see from Table 2 that increasing the sintering time resulted in a large change in density with the highest being at 1,700 °C for 20 min. 1,700 °C was the highest temperature possible for this instrument. It is felt a higher temperature would result in even higher densities. A new DCS (Direct current sintering) furnace has been ordered for Marshall Space Flight Center which will have this capability. The only difference between the SPS and DCS is that the SPS uses pulsed current rather than constant direct current.

The microstructure of one of the samples sintered at 1,400 °C for 5 min is shown in Fig. 4. Fig. 4a is a low magnification electron micrograph which shows a fairly uniform distribution of HfO₂ particles in the tungsten matrix. Fig. 4b is a higher magnification image of the tungsten matrix showing the porosity in detail. This sample had an 82% of theoretical density.

A stark comparison can be made with the samples sintered at 1,700 °C for 20 min as shown below in Fig. 5.

As can be seen from Fig. 5, the HfO₂ particles are fairly uniformly distributed within the tungsten matrix. In this instance the density was 96% of theoretical. The porosity appears more in the HfO₂ particles. This may occur since the sintering is performed in vacuum. Reduction of HfO₂ would lead to oxygen vacancy

formation with the vacancies coalescing into pores during the sintering process.

Vicker's Microhardness results are shown in Fig. 6 below. The hardness was calculated from the following equation:

$$H_v = P/A = \alpha * P/d^2 \quad (1)$$

where, P is the applied load, A is the area of applied load, d is the indent diagonal and α is a constant equal to 1.8544.

Table 2 Sintering temperature, sintering time and % of theoretical density for SPS sintered W/HfO₂/PE powders.

Sintering temperature (°C)	Sintering time (minutes)	% of theoretical density
1,400	5	82
1,500	5	85
1,500	20	91
1,600	20	93
1,700	20	96

Fig. 4 (a) 150 x and (b) 2,000 x Electron Micrograph of SPS sintered sample at 1,400 °C for 5 min.

Fig. 5 (a) 40 x and (b) 150 x Electron micrograph of SPS sintered sample at 1,700 °C for 20 min.

Fig. 6 Vicker's Microhardness values for SPS sintered samples at 1,500, 1,600 and 1,700 °C.

Fig. 7 Diagonal Microhardness indents in SPS sintered sample at 1700 °C.

The hardness was calculated for samples sintered at 1,500, 1,600 and 1,700 °C. It can be seen from Fig. 6 that the hardness increases with sintering temperature

to maximum of 312.14 kgf/mm² at 1,700 °C. This is expected since these are the densest samples. This value is in line with values for pure tungsten found in the literature. Fig. 7 shows a typical indent for the 1,700 °C sample.

It was expected that we might see diametral cracks at the tips of the diagonals, however, none were observed. Loads higher than our instrument was capable that would be needed.

It was decided that W/ UO_2 /A-C 617A powders would be sintered and microstructure studied to determine if this powder process would work as well for this system as it did for W/ HfO_2 /A-C 617A powders. In this instance powders were mixed in the same manner as the W/ HfO_2 /A-C 617A powders. The difference was that these powders were then hot isostatic

Fig. 8 Scanning electron micrograph of angular UO_2 powder in tungsten matrix.

Fig. 9 Scanning electron micrograph of spherical UO_2 powder in tungsten matrix.

pressed rather than sintered by SPS. A comparison is made in the following figures which show mixed angular UO_2 powders and tungsten powders (Fig. 8) and spherical UO_2 and tungsten powders (Fig. 9). X-ray maps for both types of samples are also shown.

As can be seen in Fig. 8, the angular UO_2 phase is not uniformly distributed within the tungsten matrix. This material was mixed in the turbula then poured directly into the HIP (Hot isostatic press) tube which would allow segregation to occur. By contrast, the material shown in Fig. 9 uses the A-C 617A binder which resulted in a more uniform distribution of the spherical UO_2 particles in the tungsten matrix.

4. Conclusions

It was found that in order to obtain a uniform

distribution of spherical HfO_2/UO_2 particles in a tungsten matrix it was necessary to use 0.5 wt.% polyethylene homopolymer as a binder. The $\text{HfO}_2/\text{W/A-C}$ 617A binder powder was densified using spark plasma sintering and resulted in a uniform mixture of HfO_2 within the tungsten matrix. The best results were obtained by sintering at $1,700^\circ\text{C}$ for 20 min which resulted in samples that were 96% of theoretical density and had a Vicker's hardness of 312.14 kgf/mm^2 . Utilizing the same powder processing technique, a uniform mixture of spherical UO_2 within a tungsten matrix was produced using hot isostatic pressing.

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