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B. O'Brien
W. E. Windes
A. E. Erickson

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Nitride Fuel Development Using Cryo-process Technique

B. O'Brien, W.E. Windes, A.E. Erickson

Idaho National Laboratory

INL Research Center

2351 N. Boulevard

P.O. Box 1625

Idaho Falls, ID, 83415-2218

Tel :208-526-6984 , Fax: 208-526-4822 , Email: William.windes@inl.gov

Abstract – *A new cryo-process technique has been developed for the fabrication of advanced fuel for nuclear systems. The process uses a new cryo-processing technique whereby small, porous microspheres (<2000 μm) are formed from sub-micron oxide powder. A simple aqueous particle slurry of oxide powder is pumped through a microsphere generator consisting of a vibrating needle with controlled amplitude and frequency. As the water-based droplets are formed and pass through the microsphere generator they are frozen in a bath of liquid nitrogen and promptly vacuum freeze-dried to remove the water. The resulting porous microspheres consist of half micron sized oxide particles held together by electrostatic forces and mechanical interlocking of the particles. Oxide powder microspheres ranging from 750 μm to 2000 μm are then converted into a nitride form using a high temperature fluidized particle bed.*

Carbon black can be added to the oxide powder before microsphere formation to augment the carbothermic reaction during conversion to a nitride. Also, the addition of ethyl alcohol to the aqueous slurry reduces the surface tension energy of the droplets resulting in even smaller droplets forming in the microsphere generator. Initial results from this new process indicate a lower impurity contamination in the final nitrides due to the single feed stream of particles, material handling and conversion are greatly simplified, a minimum of waste and personnel exposure are anticipated, and finally the conversion kinetics may be greatly increased because of the small oxide powder size (sub-micron) forming the porous microsphere. Thus far the fabrication process has been successful in demonstrating all of these improvements with surrogate ZrO₂ powder. Further tests will be conducted in the future using the technique on UO₂ powders.

I. INTRODUCTION

Nitride fuels are considered to have great potential in a variety of applications. Uranium mononitride has been considered for many applications including fast reactors, liquid-metal-fast-breeder reactors¹⁻⁴, and space reactors including the submersion-subcritical safe space reactor⁵ and the SP 100 space reactor⁶. Nitride fuels are also being considered for actinide burning, examples of these are zirconium nitride as an inert matrix fuel, (U, Pu)N, as well as other actinide mononitrides⁷⁻¹².

There are already several methods that have been used to create material feedstock for uranium nitride, such as the

sol-gel method, powder processing by carbothermic reduction and direct coagulation casting. However, with the sol-gel method, there is incomplete conversion from a carbide to a nitride. Impurities are easily introduced during powder processing methods, thus causing incomplete conversion and sintering. Direct coagulation has demonstrated problems with actinide containing material, and cannot be used for many of the applications being considered for nitride fuels.

A new method for producing advanced nitride fuel has been developed which alleviates many of the problems posed from these other techniques. This is a cryo-process using sub-micron sized particles suspended in an aqueous

slurry which is then formed into small porous microspheres via a freeze dry method. These microspheres are then converted inside a high temperature particle bed fluidizer and act as feed stock for the final fuel form.

This new process method offers many advantages over the previous techniques with the foremost being simplified material handling through the use of the larger microspheres. The limited need of handling the powders decreases potential contamination, thus improving conversion efficiency and fuel quality. Another distinct advantage is the lack of organics which can decompose under irradiation fields. This makes fabrication of actinide bearing fuel possible. Finally, the small size of the oxide particles in the microspheres promises to decrease the process time necessary for complete conversion. All of these advantages will provide an improved process method for advanced nitride fuel fabrication incorporating volatile and highly radioactive constituents.

II. Experimental

The initial studies were conducted using a ZrO₂ powder (Inframmat Advanced Materials) surrogate material in place of UO₂ or U₃O₈. After optimization of the new process method UO₂ powder will be used to fabricate the microsphere feedstock.

II.A. Slurry Suspension

For this new processing method sub-micron sized particles are suspended in an aqueous slurry, which is to be the feed stock for the microspheres. Thus far two types of slurries have been produced. One slurry type contains mainly oxide particles. The other contains not only oxide particles, but also carbon in order to assist in the complete conversion to a nitride. Slurry compositions are shown in table 1.

TABLE I
 Slurry Composition

Ingredient	Distributor	Description
ZrO ₂	Inframmat Advanced Materials	~.5µm 99.9+%
Monarch 120	Cabot Corp.	carbon black, 75 nm
Duramax B-1000	Rohm and Haas	ceramic binder
Darvan 7-N	R.T. Vanderbilt Company, Inc.	sodium polyelectrolyte
Water	N/A	nanopure water
Alcohol	AAPER Alcohol and Chemical Co.	ethyl alcohol USP 200 proof

For the oxide-carbon slurry composition a dispersant must be ultrasonically mixed with the carbon particles for five minutes to fully suspend the carbon. After suspending

the carbon particles the binder and oxide powder can be mixed in using a high sheer mixer, mixing for five minutes. All constituents for the pure oxide slurry are mixed simultaneously for five minutes using a high shear mixer.

While experimenting with the slurry it was found that there are many factors that are key to making the slurry homogeneous and with the correct consistency to be able to pump through the microsphere generator. These factors included using a hydrophilic carbon black as well as using the correct amounts of dispersant and binder.

Use of a hydrophilic carbon black product (Cabot Corp.) without additives was necessary to produce a completely homogeneous slurry suspension. The dispersant and organic binder were helpful in pumping the slurry through the microsphere generator but were not necessary for retaining the geometry of the microspheres. These were determined to be held together from electrostatic forces and/or mechanical interlocking of the sub-micron particles.

Finally, through experimentation it was found that the addition of alcohol to the aqueous solution produced smaller, more robust microspheres. It was found that microspheres formed from an alcohol-aqueous slurry kept their spherical geometry even without the addition of binders. Dust and small particulates were eliminated from powder pressing activities using these microspheres. They were even robust enough to survive service within the fluidized particle bed with minimal degradation of microspheres.

Optimization studies were conducted to determine optimal conditions for carbon suspension and slurry homogeneity via optical microscopy. Similar tests were performed to optimize the slurry without carbon. The optimal slurry mixtures, showing the particle loading are shown in table 2.

TABLE II
 Particle Loading

Ingredient	Oxide Amount (weight %)	Carbon + Oxide Amount (weight %)
Water	20.68	37.04
Alcohol	1.84	1.78
Monarch 120	0	10.86
Darvan 7-N	4.74	4.58
Duramax B-1000	2.34	2.26
ZrO ₂	70.40	43.48

II.B. Microsphere Formation

Once a homogeneous slurry was formed it was then pumped through a microsphere generator to form aqueous-

based droplets. The microsphere generator consists of a pump which feeds the slurry through a needle attached to a variable vibration generator. The pumping speed of the slurry depends on the viscosity of the slurry. As the slurry is pumped through the needle the vibration of the needle shears off the slurry droplets at the desired size with the optimum frequency and amplitude. Thus far 40 Hz and 140 mVrms have worked well for both the oxide and the carbon slurries.

The sheared off droplets fall through a settling column filled with liquid nitrogen where they are frozen into solid aqueous based spheres. To avoid the microspheres from fusing together the pump rate must be monitored to ensure that there is ample time for the microspheres to freeze before coming into contact with one another. Also, the liquid nitrogen in the settling column must be deep enough for the droplets to freeze completely before reaching the bottom of the container. If the liquid nitrogen is too shallow the droplets flatten once they reach the bottom of the column and freeze into a disc shape. In order to give the microspheres enough room to freeze while suspended in the liquid, at least 25 cm liquid height is necessary.

Non-spherical microspheres also occur when there is insufficient particle loading in the slurry. If the slurry does not contain enough solid material, the microspheres will not be able to maintain their spherical form and will collapse into an undesired disc shape.

Once the slurry droplets are frozen into a spherical form they are then placed in an insulated vacuum chamber to evacuate all liquids. Images of the microsphere generator, pump, and vacuum chamber are shown in figure 1.

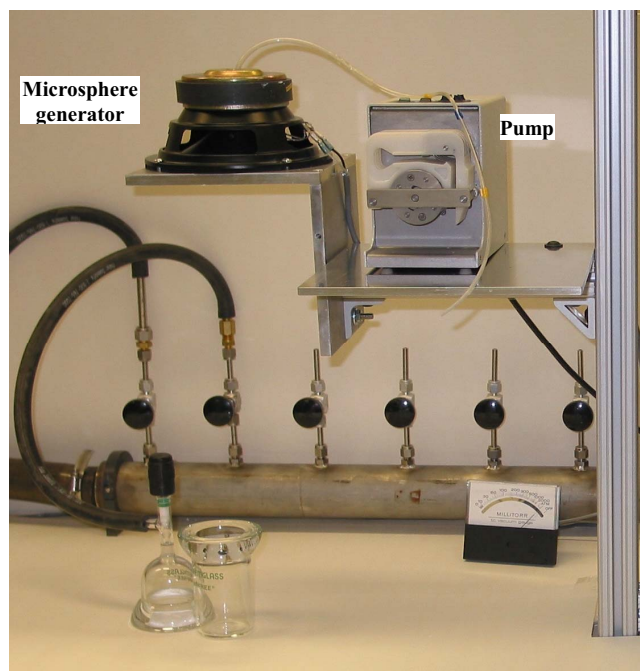


Fig. 1. Microsphere generator, pump and vacuum chamber.

The vacuum drying has proved to be a crucial step in the successful formation of the microspheres. The microspheres must be kept frozen during vacuum drying; otherwise they will not remain in their spherical form. This can be done by simply insulating the vacuum chamber. It is also necessary to keep the microspheres in the vacuum until they are completely dry. If they are prematurely removed they will fuse together.

III. Results

The cryo-formed microspheres are not perfectly spherical as seen in Figure 2. The small, porous spheres consisting of 0.5 micron particles can range in size from 750 μm to 2000 μm . Size distributions typically range from $\pm 10\%$ for each size range. Microsphere size can be adjusted by altering the slurry viscosity, needle size, and vibrational amplitude and frequency.

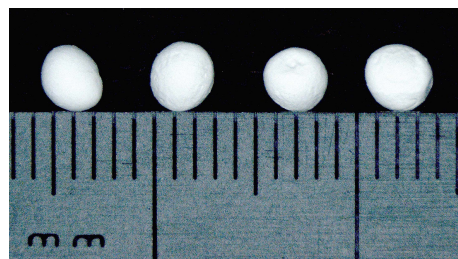


Fig. 2. Zirconium-oxide Microspheres.

These microspheres are then converted to a nitride in a fluidized gas bed through a carbothermic reaction process. Conversion efficiencies of 90%, with certainty within about 10%, have been obtained thus far, and more experiments are being performed to improve the conversion efficiency.

As the conversion process proceeds, the size of the particles decreases. Microspheres in various stages of conversion are shown in Figure 3. Once the microspheres are converted they are slightly smaller, but still porous and friable allowing them to be crushed into pellet form, one of the final forms anticipated for nitride fuel systems. The details of the fluidized gas bed and the conversion process are presented in separate papers at this conference, including more detailed information of the conversion efficiencies obtained in these experiments.

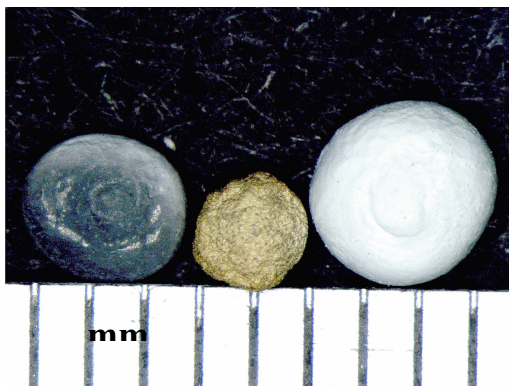


Fig. 3. Carbide, nitride, & oxide microspheres (l to r).

IV. CONCLUSIONS

A new processing technique for fabricating advanced nitride fuels has been presented that should improve on past processing techniques. The formation of larger (750-1200 μm) microspheres can greatly reduce contamination due to the limited handling of the powders through the single feed stream of particles, also limiting radiation exposure. Since this process uses a simple aqueous solution (no organics) the addition of high radiation field actinides can be achieved.

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