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Nitride Fuel Development at the INL

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A new method for fabricating nitride-based fuels for nuclear applications is under development at the Idaho National Laboratory (INL). A primary objective of this research is the development of a process that could be operated as an automated or semi-automated technique reducing costs, worker doses, and eventually improving the final product form. To achieve these goals the fabrication process utilizes a new cryo-forming technique to produce microspheres formed from sub-micron oxide powder to improve material handling issues, yield rapid kinetics for conversion to nitrides, and reduced material impurity levels within the nitride compounds. The microspheres are converted to a nitride form within a high temperature particle fluidizing bed using a carbothermic process that utilizes a hydrocarbon – hydrogen - nitrogen gas mixture. A new monitor and control system using differential pressure changes in the fluidizing gas allows for real-time monitoring and control of the spouted bed reactor during conversion. This monitor and control system can provide real-time data that is used to control the gas flow rates, temperatures, and gas composition to optimize the fluidization of the particle bed. The small size (0.5 μm) of the oxide powders in the microspheres dramatically increases the kinetics of the conversion process yielding reduced process times and temperatures. Initial studies using surrogate ZrO_2 powder have yielded conversion efficiencies of 90 -95 % nitride formation with only small levels of oxide and carbide contaminants present. Further studies are being conducted to determine optimal gas mixture ratios, process time, and temperature range for providing complete conversion to a nitride form.

I. INTRODUCTION

A new process method for producing nitride fuel is currently under development at the INL. While the advantages of nitride-based fuel forms [1, 2] are well known (high thermal conductivity, higher peak linear powers, higher heavy metal density, chemical compatibility, etc.) numerous problems have been encountered when attempting to synthesize this material system into a viable form. This new process methodology is intended to answer specific issues encountered with past production of nitride fuel forms [2-5].

The current method utilizes an oxide particle feedstock formed into larger microspheres which is converted within a high temperature particle fluidized conversion furnace. Emphasis is placed upon minimal material handling, process simplicity, minimization of impurities, and carbo-thermic conversion efficiency. It is anticipated the mixed nitride systems (Pu/UN) could especially benefit from these process improvements.

Specific attention has been focused upon creating a new material feedstock that allows for minimal handling and maximum conversion efficiency as well as in-situ monitoring of the particle bed fluidizer to optimize the conversion process. The fabrication of the material feedstock uses a cryo-process necessitating minimal contact with the powder. In-situ monitoring of the fluidizing gas pressures within the particle bed can determine the activity of the emulsion bed and changes in the fluidization behavior of the particles. This can provide a real time method for monitoring the conversion process leading to an optimized fuel chemistry stoichiometry. A final, unstated objective of this research is to determine the possibility of fabricating a nitride based feedstock material remotely utilizing these techniques.

II. RESULTS AND DISCUSSION

The new INL nitride process method addresses many of the issues encountered with previous studies; development of a simpler material feedstock, reduction of dust generation, real-time process monitoring, and reduced process times. Each of these parts of the process is briefly described. Further details of the microsphere fabrication process, the fluidizing particle bed, and the real-time monitoring capabilities are described in more detail in other papers presented at this conference.

II.A Development of microsphere feedstock material

The new INL nitride process method utilizes a cryo-process in which sub-micron sized oxide particles are formed into larger, porous microspheres which can be more easily handled, create less contamination (dust), and may provide enhanced carbo-thermic kinetics. The oxide powder is suspended in an aqueous slurry with minimal organics (binders, dispersants, or deflocculants) that can be pumped through a vibrating, small gauge needle. As the

slurry is pumped through the needle the slurry stream is sheared into droplets at the appropriate frequency and amplitude, Figure 1. The slurry viscosity, needle vibration frequency, vibration amplitude, and gauge size all contribute to the final droplet (microsphere) size.

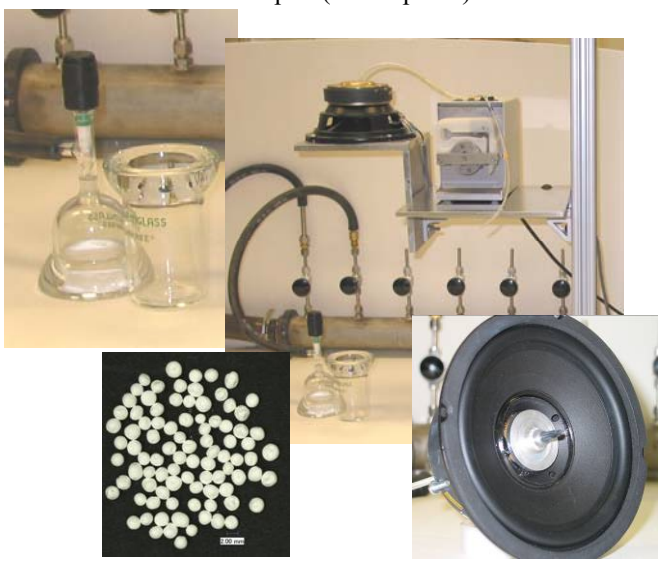

Fig. 1. Microsphere generating system illustrating (counter clock-wise) entire system, vacuum chamber, freeze-dried microspheres, and vibrating needle component.

As the slurry droplets are formed they are allowed to fall into a bath of liquid nitrogen, freezing the water-based droplets into spheres. Immediately, the microspheres are removed from the liquid nitrogen and placed within a vacuum chamber for freeze drying. A vacuum of approximately 200-300 millitorr is applied to the microspheres as the temperature is slowly raised. The final product after freeze-drying is a small (~ 1mm diameter), porous microsphere with very low crush strength. The microspheres greatly improve the handling of the material, significantly reduce any dust, and allow for easy conversion. These microspheres are used as the material feedstock for the conversion furnace described below, Figure 2.

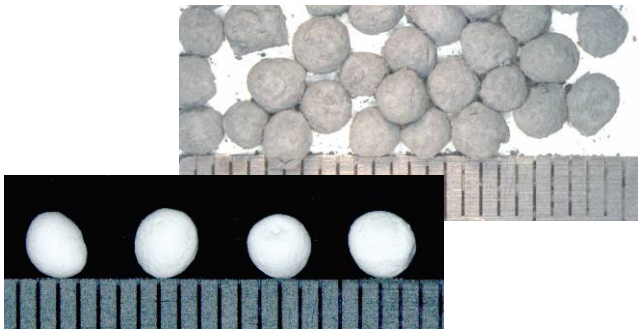

Fig. 2. Oxide and carbon-oxide microspheres fabricated using cryo-process.

It was found that the addition of a solid carbon source [4, 5] to the oxide microsphere was helpful in providing complete conversion to a nitride form. A hydrophilic carbon black powder was added to the oxide slurry and ultrasonically mixed for 5 minutes. The carbon-oxide slurry was then pumped through the microsphere generator to produce the appropriately sized microspheres. The addition of carbon black did not appear to influence the formation
or freeze-dry characteristics of the microspheres.

II.B Particle fluidizer

After forming the oxide microsphere feedstock each microsphere is converted to a nitride using a carbo-thermic reaction within a high temperature, fluidized gas particle bed. The high temperature spouted bed reactor retort consists of three vertically-oriented, concentric, radially-symmetric segments machined from a single piece of graphite, Figure 3. To date, research at the INL has been performed using a conical profile base with an included angle of 60° and a height of 51.5 mm (2.03 inches). The main chamber is a cylindrical section with a constant internal diameter of 63.5 mm (2.5 inches) and a height of 310 mm (12.2 inches).

The retort is mounted within a high temperature graphite furnace capable of operating in a temperature range from room temperature to 2300°C, depending on gas composition. The flow path through the inside of the retort is isolated from that outside of the retort to prevent particulate contamination of the furnace internals. Gas flow into the retort is controlled by four mass flow controllers operating in parallel to provide control of inlet gas composition. Exhaust gas from the retort and furnace is cooled and filtered before passing through back flow prevention check valves, flash arrestors, and the controlled oxidation igniter.

Once a gas flow rate sufficient to retain the particles in the retort reaction zone (conical base and cylindrical main segments) has been set, the particles in the gravity-feed particle loading system, positioned above the retort, are dumped directly into the retort. Particles are removed from the retort by decreasing the gas flow rate below the terminal velocity value, which allows the particles to fall through the retort inlet, past the horizontally-oriented inlet gas supply port, and into a particle collection vessel positioned directly underneath the retort outside of the furnace.

II.C Data Acquisition and Control System

Due to the opacity of the high-temperature retorts and process gases any optical monitoring of the progress of conversion is impossible. However, the particle bed activity may be directly measured using back pressure data

from the retort inlet gas flow. These pressure fluctuations within the conversion reactor can reveal information regarding the particle size, density, and spouting regime of the particle bed. This information can be used to determine and control coating/conversion parameters and adjust input parameters.

In order to measure these pressure fluctuations in the gas flow, a real time, high-frequency monitoring system was developed. Pressure fluctuation data was then correlated to visualization data obtained from an optically clear "mockup" retort which was geometry identical to that of the high-temperature retort.

Spouted bed temperature monitoring and control is achieved through use of a Eurotherm temperature controller and a Type C thermocouple reaching from the top of the furnace into the hot zone of the particle retort. Differential pressure across the particle bed is monitored through a differential pressure transducer plumbed into the gas inlet tubing. The low pressure side of the transducer is plumbed into the retort exhaust gas outlet tubing.

A high-speed data acquisition board is used for data capture and process control. Signal processing and data analysis is accomplished with a software user interface written at the Idaho National Laboratory using National Instruments LabVIEW 8.0 software. A National Instruments CA-1000 shielded enclosure containing one SCB-68 and one CB-68 LPR connector block, both supplied by National Instruments, serves as the interface between the temperature, pressure, and flow monitoring and control hardware and the data acquisition board.

II.D Conversion process

Previous research on nitride fuel fabrication has developed various nitride processing schemes. The two primary methods for converting a metal to a nitride form are hydriding-nitriding of pure metal or carbo-thermic reduction / nitriding of oxides using a wide variety of techniques. This research uses a carbo-thermic-reduction / nitriding process to support the general emphasis on processing simplicity, ease of handling, cost, and time. The INL conversion process follows the general reactions:

$$\begin{aligned} &UO_2 + 3C \leftrightarrows UC + 2CO \\ &UC + \tfrac{1}{2}N_2 \leftrightarrows UN + C \\ &C + 2H_2 \leftrightarrows CH_4 \end{aligned} \qquad (1)$$

As seen, the principle intent is to strip away any contaminant (i.e. primarily oxides or carbides) from the pure metal to allow complete nitride formation of the metal. Oxides are tenacious and an energetically more favorable form of the metal. It is difficult to completely strip it from the metal and thus remaining oxides provide the main contamination issue for nitride conversion. Removing the oxide requires exposing the microspheres to fairly high temperatures as well as a reducing, carbon-rich atmosphere before carbides will start to form. Complete carbide formation is usually necessary before a nitride can be formed.

At first, the approach was to take advantage of the high porosity in the new oxide microspheres utilizing only a carbon-rich, hydrogen-rich gas environment inside the fluidized particle bed. It was assumed that the relatively short diffusion distances into the oxide powder (nominally 0.5 μm diameter) would allow rapid and nearly complete conversion of the oxide material without the use of carbon solids as required with past, more traditional, methods. The short diffusion distances were also assumed to reduce the kinetics of the conversion process and allow shorter times necessary to provide complete conversion.

Various hydrocarbon (CH_4) and reducing gas (H_2) compositions were used in conjunction with the fluidizing gases to provide the necessary constituents for conversion. However, the highest conversion levels achieved using these hydrocarbon gases was only about 50%. It was determined that a solid form of carbon (i.e. fine graphite powder) was required to be in direct contact with the oxide powders in order to achieve higher conversion efficiencies.

Powder slurries with hydrophilic carbon black powder were subsequently fabricated to provide these carbon containing microspheres. Then, using a combination of hydrocarbon gases and solid carbon particles within the microspheres higher carbide conversion efficiencies were achieved. Once the carbide was formed the process atmosphere was changed to nitrogen to allow nitriding of the metal to take over. Process parameters for these successful conversion runs ranged from 1450 ºC to 1650ºC over time periods as low as 2 to 4 hours, see Table 1.

TABLE I
Parameter ranges used for INL conversion process.

Process Temp., ºC	Time at temp., min.	Gas Compositions, vol%			
		CH_4	H_2	N_2	Ar
1450	60	0.5	1	50	remain.
1500	90	1	3	75	remain.
1550	120	3	4	80	remain.
1600	180	5	5	90	remain.

Carbo-thermic conversion of zirconium-oxide microspheres using the high temperature particle bed system and process parameters described above has achieved efficiencies of 95% ±5%, see Figure 3.

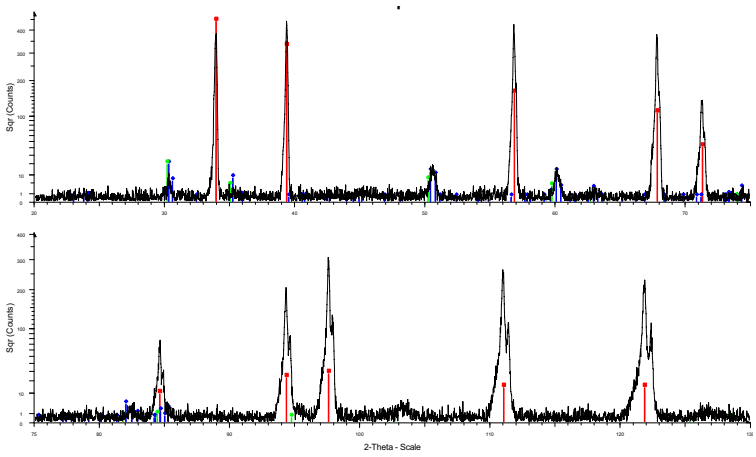

Fig. 3. XRD results for fully converted zirconia microspheres (■ – ZrN, ● – ZrO_2, ♦ - ZrO).

While some sintering and densification occurs within the microspheres during processing they are still friable and minimal effort is required to return them to a powder form for pellet pressing if desired. Microspheres at various stages of conversion are shown in Figure 4.

Fig. 4. From left to right, microspheres of a) carbide, b) nitride, and c) oxide.

III. CONCLUSIONS AND FUTURE WORK

Small, porous microspheres have been successfully fabricated using a new cryo-forming processes. These microspheres have been shown to eliminate dust and powder during processing, provide simplified handling of feedstock, and yet remain very porous/friable for rapid and complete conversion. The new fluidizing particle bed system simplifies the conversion process considerably. The microspheres are simply poured into the fluidizing retort, the processing gases act both to suspend and convert the microspheres to a nitride form. The real-time monitoring provides a superior method of monitoring the progress of conversion and the activity of the microspheres during processing. This monitoring system may be used to determine when the microspheres have been completely converted rather than empirically deriving this time. Finally, the new material feedstock and fluidizing equipment can provide a nearly complete conversion of the oxide powder to a nitride form.

Future work will focus upon fabricating microspheres with no organic material (i.e. binders) to determine the viability of using this process in producing actinide bearing material. Further, volatile surrogates will be added to allowing investigation of mixed nitride or even mixed oxide microspheres to be fabricated. Finally, depleted uranium oxide microspheres will be fabricated in the near future to verify these process improvements are applicable to the uranium material system.

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