

Sol-gel Micro- Mini-Sphere Development

Stewart Voit
Oak Ridge National Laboratory

1. Introduction

The Advanced Fuels Campaign ceramic fuels R&D effort, within The Department of Energy Fuel Cycle R&D Program, has undertaken an R&D approach that integrates fundamental R&D on ceramic fuel feedstock, fuel fabrication development, and separate effects irradiation testing. The goal is to achieve a fundamental understanding of the inter-relationships that exist between nuclear fuel materials properties, processing, and performance.

In parallel with this type of basic research, it is important to advance the state of the art with respect to processing of nuclear fuel materials that must be handled in a controlled environment. Toward that end, it is important to consider ways to minimize processing losses associated with the synthesis and fabrication of nuclear fuel. One option may be to transition away from the standard powder-type fuel synthesis and pellet fabrication process and to use flowable, near-dustless spherical particles that can be pressed directly into pellets thus avoiding the use of dust generating milling and blending processes.

2. Sol-gel micro-, mini-sphere development

The goal of this work is to evaluate the use of the sol-gel (internal, external) technology to produce near-dustless spherical particles for use as a potential oxide feedstock to support the oxide fuel development effort. The work package scope was refocused when the urania/surrogate sol-gel infrastructure was dismantled to make way for the refurbishment of lab space in building 4501. As a result, the experimental balance of the spherical particle work package (sol-gel/resin) shifted toward the synthesis of spherical particles using a cation exchange resin (see ORNL/TM-2010-216) and the sol-gel effort concentrated on planning for FY11.

The sol-gel planning effort began with a survey of the literature for relevant work. Solution based routes for the production of spherical particle fuels have been investigated since the 1960s with the demonstrated ability to form oxide microspheres of controlled size and shape; however, little work has been done investigating the direct pressing of sol-gel particles.

In the 1960's, Ferguson, et al prepared UO_2 and $\text{UO}_2\text{-Gd}_2\text{O}_3$ pellets at ORNL from particles synthesized using the sol-gel technique.¹ Their study evaluated pellet density and microstructure as a function of sol-gel particle reduction and pellet sintering conditions. The authors conclude that the sol-gel particles have high sinterability producing dense pellets however, when sintered into pellets, the near fully dense particles created a "blackberry" microstructure with open pores because

the microspheres retained their individual identity during pressing. An example of the blackberry-type microstructure is shown in Figure 1.

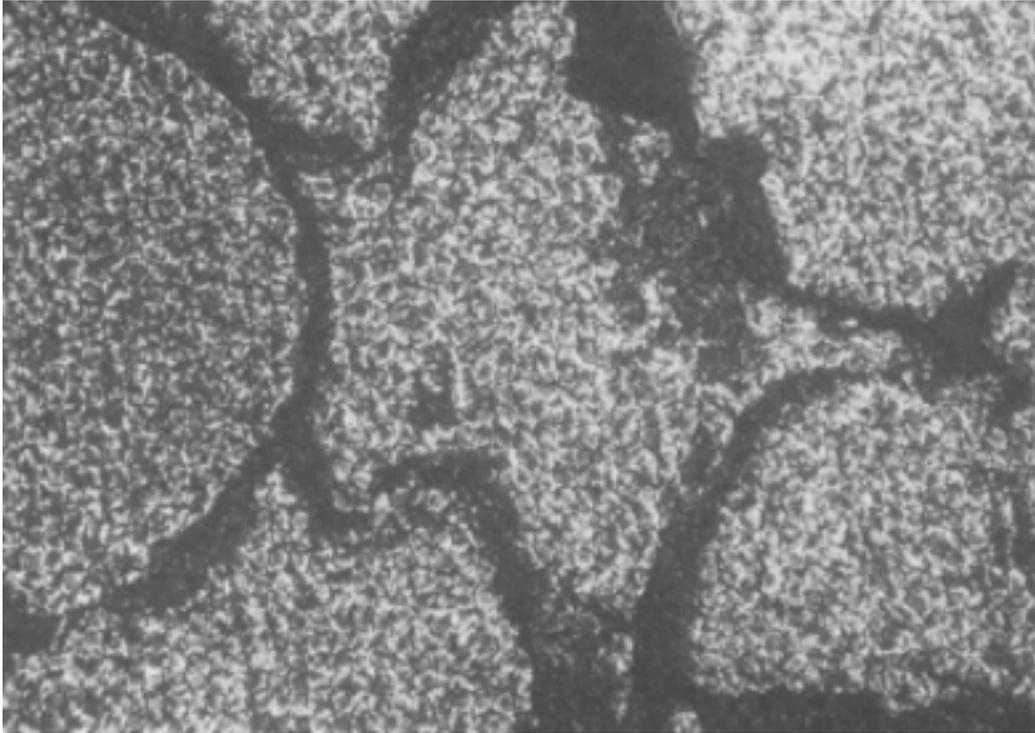


Fig. 1. Typical blackberry structure formed by direct pressing and sintering of dense sol-gel particles.

In the mid 1990s, researchers at the CEA and PSI collaborated on seminal R&D related to crushable sol-gel particles for pellet fabrication.ⁱⁱ They studied the fabrication of what they termed “hybrid” pellets using mixed actinide nitride sol-gel microspheres. Of particular interest is their research on weakening the microstructure of the spheres prior to pressing. They found that structural properties were influenced by the reaction atmosphere and that the formation of a porous, interlaced microstructure provided the best results when measuring particle crush strength.

The FY11 sol-gel effort at ORNL will follow a similar experimental approach beginning with urania. As-synthesized urania sol-gel particles are hexa-valent UO_3 . The UO_3 will be reduced to UO_2 and the conditions under which the reduction is performed will be the primary area of focus. Process variables such as temperature, atmosphere, and process additives will be considered. Also employed will be the use of boiled hexamethylenetetramine (HMTA)-urea stock solutions to control crystallite growth. This method has been successfully demonstrated by Collins et al.ⁱⁱⁱ

The sol-gel synthesis/reduction parametric study will be followed by detailed characterization of particle characteristics. X-ray diffraction will be used to confirm

the phase of the final product. Laser diffractometry and the Brunauer-Emmett-Teller method will be used to determine particle size and surface area respectively. Gas pycnometry and mercury porosimetry measurements will be used to characterize particle envelop density, skeletal density, and surface connected porosity. Electron microscopy will be used to reveal microstructural features and a point load system will be used to measure particle crush strength. Finally, samples from select particle batches will be sent to LANL for studies of the pressibility and sinterability.

3. Conclusion

Porous microspheres made from the sol-gel process show considerable promise as a low-process loss alternative to the present powder-based ceramic feedstock. Previous work has demonstrated that microspheres are flowable and it may be possible to press the spherical particles without the need for milling and blending. Due to the refurbishment of the lab space housing sol-gel process equipment, FY10 spherical particle research at ORNL shifted from R&D centered on the use of sol-gel particles as a potential ceramic fuel feedstock to an emphasis on the resin-loading method for synthesizing spherical particles. As a result, the present sol-gel effort focused on planning. The reinstallation of internal gelation capability begins the final week of September 2010. The particle characterization resources are in place and ready to support the FY11 spherical particle R&D effort.

ⁱ Ferguson, D., et al., Metal Oxide Microspheres from Ion Exchange Resins, CEND-153, Vol. 1, p 23, (1963), ORNL/TM-53.

ⁱⁱ Ledergerber, G., et al., Nuclear Technology, Vol. 114, p 194-203, (1996).

ⁱⁱⁱ Collins, J., et al., Control of Urania Crystallite Size by HMTA-UREA Reactions in the Internal Gelation Process for Preparing (U, Pu)O₂ Fuel Kernals, ORNL/TM-2005-10.