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Impact of the Synthesis Process on Structure Properties for AFCI Fuel Candidates

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Student Research Proposal under UNLV TRP

Title

Impact of the Synthesis Process on Structure Properties for AFCI Fuel Candidates

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Technical Focus Area

Fuels (Fabrication and Structure Properties)

Abstract

Transmutation work at Los Alamos National Laboratory is currently focused on mono-nitride ceramic fuel forms, and consists of closely coordinated “hot” actinide and “cold” inert and surrogate fuels work. Matrix and surrogate materials work involves three major components: (1) fuel matrix synthesis and fabrication, (2) fuel performance, and (3) fuel materials modeling. The synthesis and fabrication component supports basic

material studies, as well as actinide fuel fabrication work through fuel fabrication process development. Fuel performance studies are examining the tolerance of nitride-type fuel to heavy irradiation damage. The fuel materials simulation work involves both atomistic and continuum scale modeling employing first principals, molecular dynamics, and thermo-chemical calculations. This modeling work is closely integrated with fuel design and experimental work where it provides prediction of phase transformation and stability, reaction kinetics, radiation damage mechanism and tolerance, and fission product retention. Results for fuel fabrication and radiation tolerance studies based on the proposed ZrN fuel matrix material will be reviewed as well as experimental surrogate studies for volatilization and phase stability. The actinide fuel effort at LANL emphasizes in synthesis and fabrication of actinide-bearing nitride fuel pellets. These pellets are designed for being inserted into the Advanced Test Reactor and contain varying amounts of Pu, Am, Cm, and Np.

For now, fuel materials simulation work which involves atomistic and continuum scale modeling, molecular dynamics, and thermo-chemical calculations is purely based on a theoretical understanding of crystal structure and microstructure of inert matrix fuels. We intent to support the AFCI program by delivering real structural data on surrogate and radioactive fuels. We will determine crystal structure and nano structures of the individual fuel type, oxides and nitrides, as considered for GEN IV fuels. Furthermore we will mainly apply two different ways to synthesis fuels: (1) wet chemical route (precipitation from solution, calcinations, grinding, pelletization, sintering with binder and PEG, grinding, pelletization, and sintering with carbon-thermal reduction (later for nitride fuels only), and (2) dry chemical route (grinding of oxides, pelletization, sintering with binder and PEG, grinding, pelletization, and sintering with carbon-thermal reduction (later for nitride fuels only). The chemical behavior of the ceramics under repository, reprocessing, and reactor conditions will also be examined. This data will provide the basis for a full analysis of the fuel in an advanced fuel cycle.

We will analyze the impact of fuel processing parameters on the crystal structure and nano structure of the inert matrix fuel desired for GEN IV reactors. Therefore we will - beside other analytical techniques - mainly apply (1) X-ray powder diffraction (XRD) in combination with Rietveld structure refinement to refine or to determine actinide occupancies within the crystal lattices of the fuels, and (2) high resolution electron microscopy (transmission electron microscopy) in combination with, nano probe X-ray spectrometry (EDS), parallel energy loss spectroscopy (PEELS), energy-filter electron microscopy, and scanning transmission electron microscopy. We will use state-of-the-art analytical instrumentation on X-ray diffraction (PANalytical X-Pert Pro with X'Cellerator solid state detector and Bruker AXS Topas2 Rietveld structure refinement software), and high resolution electron microscopy (Tecnai F 30 STEM with a FEG field emission gun, scanning option, PEELS, EDS, Energy-Filter, 300 kV acceleration, and a point resolution of 2.2 Å). We can take advantage of two fully equipped sample preparation laboratories, one for the preparation of surrogate fuel, one for the preparation of radioactive fuel specimens. The analytical work scope as proposed will promote the Harry Reid Center for Environmental Studies of UNLV as the top academic institution in the U.S. for analyzing radioactive fuel samples on nano-scale.

X-ray absorption fine structure spectroscopy (XAFS) will also be used in analysis. XAFS includes EXAFS (extended x-ray absorption fine structure spectroscopy) and

XANES (x-ray absorption near edge spectroscopy). EXAFS is an atom-specific local structure probe used to determine the molecular structure of a species. Data can yield information including average interatomic distances and the number and chemical identities of neighbors within 5 to 6 Å of a selected atom species. XANES data contains information on bound state electronic transitions and is used to determine the oxidation state of the species.

Evaluating the chemical behavior of the ceramics will be performed in batch samples under controlled atmosphere conditions. Solution samples are periodically removed and the solution concentration of the ceramic components determined by ICP-AES, ICP-MS, or alpha spectroscopy. The expected conditions will be

- Elevated water temperature conditions (90 °C to 350 °C)
- Nitric Acid Conditions (2-12 M, 25 °C to 90 °C)
- Near neutral solution conditions under CO₂ from 25 °C to 80 °C

Dissolution studies will be performed on the ceramics under a variety of conditions in order to collect relevant and applicable thermodynamic data. Dissolution variation with temperature evaluated to assess enthalpy, entropy, and Gibbs free energy. The excess ceramic material in each flask will be examined following the dissolution study using the previously described techniques and compared to pre-dissolution data to determine any changes in chemistry of the surface or bulk.

XAFS includes EXAFS (extended x-ray absorption fine structure spectroscopy) and XANES (x-ray absorption near edge spectroscopy). EXAFS is an atom-specific local structure probe used to determine the molecular structure of a species. Data can yield information including average interatomic distances and the number and chemical identities of neighbors within 5 to 6 Å of a selected atom species [i]. In contrast, XRD gives the general phase composition of the crystal, such as U_{0.2}Th_{0.8}O₂. XANES data contains information on bound state electronic transitions and is used to determine the oxidation state of the species.

Scientific Investigation Plan

We are proposing the following research work:

Academic year 2005

1. Set-up sample preparation equipment for surrogate fuel samples, establish and further optimize sample preparation procedure for electron transparent surrogate fuel specimens to suit the purpose of high resolution electron microscopy.
 - a. Develop a SOP (standard operation procedure) for the use of the following instrumentation: low-speed saw (Buehler), ultra-sonic disc cutter (Gatan), grinder and polisher (Buehler), multi-preparation system (Allied), sample dimpler (South Bay Technology), and ion-mill (Fishione).
 - b. Optimize sample preparation procedure on the individual equipment on ceramic surrogate oxide Cer and Ceric fuel pellets.
 - c. Optimize sample preparation procedure on the individual equipment on ceramic surrogate nitride Cer and Ceric fuel pellets.

- d. Compare with sample preparation by Ultra-microtome.
2. Set-up and perform initial dissolution experiments on actinide oxides
3. Literature research on:
 - a. GEN IV reactor fuel to come.
 - b. High burn-up fuels (e.g. TRISO)
 - c. Inert Fuel Matrix (IMF) fuels as proposed within the international community.

Academic year 2006

1. Develop and refine a wet-chemical route for synthesizing surrogate and radioactive oxide fuel pellets in the phase constitutional system $ZrO_2 - Er_2O_3 - UO_2 - ThO_2 - PuO_2 - MgO$
2. Develop and refine a wet-chemical route for synthesizing surrogate and radioactive nitride fuel pellets in the phase constitutional system $ZrN - ErN - UN - ThN - PuN - Mg_3N_2$
3. Refine the dry-chemical route for synthesizing surrogate and radioactive oxide fuel pellets in the phase constitutional system $ZrO_2 - Er_2O_3 - UO_2 - ThO_2 - MgO$
4. Refine the dry-chemical route for synthesizing surrogate and radioactive nitride fuel pellets in the phase constitutional system $ZrN - ErN - UN - ThN - Mg_3N_2$
5. Performed dissolution experiments on synthesized materials.

Academic year 2007

1. Analyze and compare the phase constitution of sintered pellets after applying the different developed procedures to synthesize surrogate oxides and surrogate IMF nitride fuels by:
 - a. X-ray powder diffraction
 - b. Rietveld structure refinement
 - c. EPMA Electron Probe Microanalysis
 - d. Differential Thermal Analysis
 - e. XAFS
2. Analyze and compare microstructure and nano structure of surrogate fuel pellets after applying the different developed procedures to synthesize oxide and nitride IMF fuels by:
 - a. SEM Scanning Electron Microscopy (micro structure)
 - b. High Resolution Electron Microscopy (nano structure)
 - c. TEM nano probe analysis EDS

- d. TEM nano probe analysis PEELS
 - e. TEM energy filter microscopy
 - f. STEM Scanning Transmission Electron Microscopy
3. Performed dissolution experiments on synthesized materials under repository, reprocessing, and reactor conditions

Academic year 2008

1. Conclude and discuss the results of the research work performed by:
 - a. Presentation on international conferences
 - b. Publication in peer reviewed international scientific papers
 - c. Technical reports of the Harry Reid Center.
2. Defend Thesis

i .Brown, Gordon E. Jr.; Waychunas G. A. X-ray Absorption Spectroscopy: Introduction to Experimental Procedures. Stanford Synchrotron Radiation Laboratory XAS Procedures, 3/11/99