

Task 28

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

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BACKGROUND

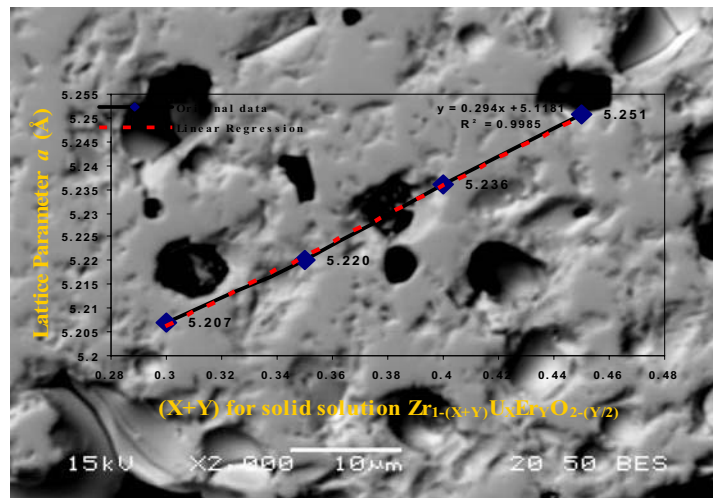
Advanced Fuel Cycle Initiative research on transmutation fuels includes mono-nitride ceramic fuel forms, and consists of closely coordinated “hot” actinide and “cold” inert and surrogate fuels work. Matrix and surrogate materials work involves three major components: (1) fuel matrix synthesis and fabrication, (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 principles, 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 synthesis and fabrication of actinide-bearing nitride fuel pellets. These pellets are designed to be inserted into the Advanced Test Reactor and contain varying amounts of Pu, Am, Cm, and Np.

Presently, fuel materials simulation work which involves atomistic and continuum scale modeling, molecular dynamics, and thermo-chemical calculations are based on a theoretical understanding of crystal structure and microstructure of inert matrix fuels. This task’s contribution is to provide real structural data on surrogate and radioactive fuels. Crystallographic properties are being determined and nano structures of oxide-based and nitride-based fuels, as considered for next generation reactor fuels, are being imaged after applying different synthesis routes. The chemical behavior of the ceramics under repository, reprocessing, and reactor conditions will be examined. Two fully equipped sample preparation laboratories can be taken advantage of, one for the preparation of surrogate fuel, and one for the preparation of radioactive fuel specimens.

RESEARCH OBJECTIVES AND METHODS

The research objectives are:

- Installation of sample preparation equipment for radioactive fuel samples to allow the manufacture of high quality polished microscopy samples and electron transparent TEM specimens.
- Literature research on Inert Fuel Matrix (IMF) fuels.
- Optimized synthesis of oxide fuels in the system $ZrO_2 - Er_2O_3 - UO_2$.



Oxide fuel sample in the system Zr-U-Er-O by Scanning Electron Microscopy, BES, 2,000 times magnified. The oxide fuels do not contain domains or impurities. The lattice parameter a in the solid-solution phases $Zr_{1-(x+y)}U_xEr_yO_{2-(y/2)}$ increases linearly with the substitution of uranium and erbium for zirconium.

- Synthesis of nitride fuels in the system ZrN-ErN-UN by carbothermic reduction / nitridization.

RESEARCH ACCOMPLISHMENTS

Zirconia-based Ceramic Fuel in the System ZrO_2 - $ErO_{1.5}$ - UO_2

Oxide fuels have been successfully synthesized in the system ZrO_2 - UO_2 - $ErO_{1.5}$ as phase-pure solid-solution phases of $Zr_{1-(x+y)}U_xEr_yO_{2-(y/2)}$ for $0.3 < (x+y) < 0.45$. The oxide phase $Zr_{1-(x+y)}U_xEr_yO_{2-(y/2)}$ is showing a linear increase in the lattice parameter as the substitution of U+Er for Zr progresses and the lattice parameter a increases from 5.2070(3) Å for $(x+y)=0.3$ to 5.2507(3) Å for $(x+y)=0.45$.

Prototype Zirconia-based ceramic fuel in the System ZrO_2 - $ErO_{1.5}$ - UO_2 was produced through dry chemical processing. The synthesis was completed after annealing at 1700°C for 24 hrs to 48 hrs in inert/reducing atmosphere.

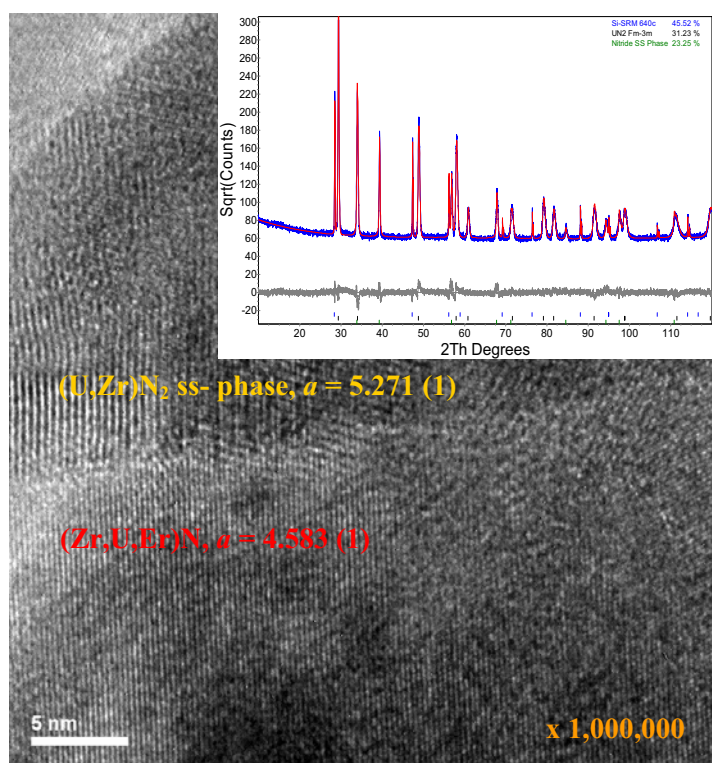
Ceramic Nitride Fuel in the System ZrN-ErN-UN

The synthesis of radioactive nitride fuel in the system ZrN-ErN-UN through carbothermic reduction/nitridization led to the formation of a ZrN-based solid solution phase and UN_2 -based solid solution phase, indicating different affinities of zirconium and uranium to nitrogen. An electron-transparent TEM specimen was prepared and the structure of the ceramics could be imaged with highest resolution. Ceramic ZrN surrogate fuel samples (provided by LANL) were analyzed by TGA/DSC thermal analysis in the temperature range of 25°C to 1400°C in N_2 atmosphere, and

changes in phase constitution and crystal structure were analyzed by XRD-Rietveld analysis and by TEM. One of three ZrN samples exhibited an exothermal reaction at about 1169°C while all samples gain about 1% in weight associated with the formation of Zr₂ON₂ and increased cubic zirconia contents.

Ceramic Nitride Fuel in the System ZrN-ErN

The carbothermic reduction / nitridization of Zr_{0.7}Er_{0.3}O_{1.85} lead to the formation of Zr_{1-x}Er_xN (lattice parameter $a = 4.6085(3)$ Å) and (Zr_{1-x}Er_x)₂(N,O)₃ (lattice parameter $a = 10.940(1)$ Å). As a result, the solubility e.g. of rare earth elements in nitrides is significantly lower than in the precursor oxide system, which can result in phase separation while applying carbothermic reduction / nitridization. In order to closer study and to quantify these phenomena focus was placed on solubility limits of erbium (a designated neutron poison) in zirconium nitrides. The solubility limit of erbium in zirconium-mononitride surrogate fuel at 1700°C was determined. Therefore a mono-phase Zr_{0.7}Er_{0.3}O_{1.85} precursor oxide-solid solution was synthesized and treated at 1700°C for 20h in purified nitrogen atmosphere. The phase constitution and the



High resolution image of Zr-Er-U-N ceramic nitride fuel after carbothermic reduction/nitridization of an oxide solid solution. An interface between two solid solution phases can be observed. The radioactive ceramic TEM sample was prepared using an ultra-microtome. The phase constitution was confirmed by XRD/Rietveld Analysis and the crystallographic parameter refined. The image is 1,000,000 times magnified.

ACADEMIC YEAR HIGHLIGHTS

- ◆ G.W.C. Silva, T. Hartmann, K. Czerwinski, "Synthesis and characterization of GEN IV reactor fuels," 231st ACS National Meeting, Atlanta, GA, March 26-30, 2006.
- ◆ K.S. Holiday, T. Hartmann, K. Czerwinski, "Zirconium-Magnesium oxides as inert matrix fuels," 231st ACS National Meeting, Atlanta, GA, March 26-30, 2006.
- ◆ S.L. Voit, K.J. McClellan, C.R. Stanek, J.T. Dunwoody, T. Hartmann, S.A. Malloy, S.P. Willson, G.E. Egeland, R.W. Margevicius, H.T. Hawkins, "The Design and Production of Nitride Fuels for the AFCI Program," *Proceedings of Global 2005*, Tsukuba, Japan, October 9-13, 2005.
- ◆ C.R. Stank, K.J. McClellan, J.T. Dunwoody, R.W. Margevicius, T. Hartmann, "Optimization of Nitride Fuel Processing through Surrogate Experiments," *Global 2005*, Tsukuba, Japan, October 9-13, 2005.

phase compositions of the equilibrium phases were determined quantitatively using XRD/Rietveld analysis and especially electron microprobe analysis. The impact of erbium solubility on the crystallographic parameter of ZrO₂ and ZrN was determined. Four samples of the solid-solution phase Zr_{1-x}Er_xO_{2-x/2} for 0.02 < x < 0.12 were synthesized and their lattice parameter were determined by XRD/Rietveld analysis. The solid solution phases in the system Zr_{1-x}Er_xO_{2-x/2} were treated by carbothermic reduction/nitridization to further determine the impact of erbium solubility on the crystallographic parameter in ZrN-based mononitrides. The phase constitution of the mononitride system Zr_{1-x}Er_xN was determined. The solubility limit for erbium in the system Zr_{1-x}Er_xN was measured to be 0.07 < x < 0.10.

Production of TRISO-type fuel kernels by Sol-Gel Method

The first spherical precursors for the potential production of TRISO-type kernels could be produced and - after calcination - kernel sizes between 400 nm and 320 nm were measured. For now the spheres show poor isotropy. Some kernels are hollow and the overall kernel quality has to be improved much further.

FUTURE WORK

The next phase of the project involves accomplishing the following tasks:

- Determine solubilities and phase constitution in the system ZrN-ErN-UN.
- Optimize TEM sample preparation to be able to perform PEELS spectroscopy.
- Improve fuel synthesis applying wet-chemical processing (including particle fuel).
- Study fuel corrosion under different scenarios.
- Determine impact of heavy ion-irradiation to fuel properties.

Research Staff

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