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Transmutation-related research work at the National Laboratories, e.g. Los Alamos National Laboratory, is 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.

This project, task 28, supports the TRP program by delivering structural data on surrogate and radioactive fuels. Crystal structure and nanostructures of the individual fuel type, oxides and nitrides, as considered for GEN IV and HTR fuels are being determined. Therefore, three different approaches on fuel synthesis will be applied: (1) dry chemical route, (2) wet chemical route, and (3) sol-gel microsphere pelletization (SGMP) process.

Work performed in current quarter (January 2006 to March 2006)

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

Efforts to optimize the experimental set-up for precipitating spherical precursors for the production of TRISO-type kernels have been intensified. After the installment of a highly accurate peristaltic pumping unit, uranyl-hydroxide-based microspheres with 0.5 mm – 1.0 mm diameters could be precipitated. Therefore a 1.49 M uranyl nitrate solution was injected into the sol-gel reaction column and uranyl-hydroxide-based microspheres could be precipitated (Figure 1). However, the kernels of the first batches did not survive the drying procedure, probably as a result of poorly chosen parameter, e.g. uranyl-hydroxide concentration, temperature, dropping speed, atmosphere. To further optimize the experimental set-up for the production of TRISO-type kernels, 3 M and 1.49 M uranyl nitrate concentrations were used to precipitate TRISO spheres. Uranyl-hydroxide-based microspheres could be precipitated but the result after drying was unsatisfactory and the spheres did not survive the drying procedure. In another batch experiment a 1 M uranyl nitrate concentration was used to precipitate precursor TRISO spheres (molar ratios of UO_2(NO_3)_2 to NH_4NO_3 to urea = 1 : 2.5 : 4). As a first success, some microspheres survived the drying procedure in wet atmosphere and changed their color to orange. The
dried spheres were calcined at 400°C for 3 hours, but only few spheres survived calcination. 

The first spherical precursors for the potential production of TRISO-type kernels could be produced and - after calcination - kernel sizes between 400 µm and 320 µm were measured (Figure 2). For now the spheres show poor isotropy. Some kernels are hollow and the overall kernel quality has to be improved much further.

Electron Energy Loss Spectroscopy (EELS) on Fuel Samples

Electron energy loss spectroscopy (EELS) was applied on radioactive fuel samples. Specimens were obtained after the carbothermic reduction/nitridization of precursor oxide solid solutions in the system ZrO2-UO2-ErO1.5. The sample constitution is defined by the presence of a ZrN-based mononitride solid solution phase and a U(O,N)2-based dioxide/dinitride solid solution phase. Electron-transparent specimen of the radioactive samples was able to be provided by dimpling and ion-milling (Figure 3a, 3b) and EELS spectra were obtained with nanometer spatial resolutions (Figure 4). However, at the current state EELS did not provide enough decisive information to distinguish oxides from nitrides. Since the EELS results are, for now, non-conclusive and published data are not available, in-house expertise as well as a data base of mono-phased zirconium and actinide standards must be developed in order to evaluate EELS spectra and to determine the presence of oxides, oxonitrides, and nitrides.

Figure 1: UO3 x H2O TRISO-type fuel kernel precipitated applying a Sol-Gel method with external gelation

Figure 2: U3O8 fuel kernels after calcination (400°C, 3 h)
The capability of the determination of oxygen and nitrogen contents in fuel samples as synthesized by the individual procedures is decisive for the evaluation and optimization of the process parameter in the synthesis of pure nitride ADS fuels. The oxygen content of ADS nitride fuels shall not exceed 3000 ppm = 0.3 wt.-%. In this context X-ray photoelectron spectroscopy (XPS) was applied on radioactive fuel samples (Figure 5). Specimens were obtained after the carbothermic reduction/nitridization of precursor oxide solid solutions in the system ZrO₂-UO₂-ErO₁.₅. The sample constitution

**X-ray Photoelectron Spectroscopy (XPS) on Fuel Samples**

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The XPS pattern of the nitride-based fuel sample is dominated by the intense bands of U 4f7/2, Zr 3d, Er 4d, and the band of O 1s. After sputtering the surface with Ar, the N 1s band became visible, but the O 1s band never disappeared. The 1s band of nitrogen shows very low intensities and the N 1s band is overlayed by one of the intense 4f band of uranium (Figure 5, right image). Using XPS and the accurate determination of the energies for the U 4f bands it is - in principle - possible to distinguish UO2 from UN. Literature data show that the binding energies of the U 4f bands in UN are lower than the corresponding bands on UO2 by 1.2 eV or 2.7 eV. Unfortunately, the XPS equipment is located at the DRI and intensified studies on pure uranium system to begin with are associated with administrative hurdles. For now the XPS measurements on solid-solution systems cannot be understood without knowledge of the pure calibrated systems.

**Carbothermic Reduction / Nitridization of Zr1-xErxO2-x/2**

In order to gain a better understanding of carbothermic reduction / nitridization to synthesize nuclear mononitride fuels the uranium-free system Zr-Er-O (-N) were studied. Fully stabilized zirconia Zr0.7Er0.3O1.85 was synthesized and used as precursor. Zr0.7Er0.3O1.85 was annealed for 20 h in a tantalum-lined high temperature furnace at 1700°C under oxygen-purified ultra-high pure argon.

Carbothermic reduction / nitridization of Zr0.7Er0.3O1.85 leads to the formation of Zr1-xErxN (lattice parameter a = 4.6085(3) Å) and (Zr1-xErx)2(N,O)3 (lattice parameter a = 10.940(1) Å)(Figure 6). As a result we were able to synthesize Zr-Er-mononitride. The solubilities for erbium in the obtained Zr-based mononitrides define the solubility limit of Er in ZrN since the precipitation of a secondary Er-rich phase was determined. As an observation, the solubility limits of erbium in Zr-mononitrides are far lower than in zirconia. This finding on lower solubility limits in mononitrides compare to dioxides is
important since it strongly influences the allowable chemical constitution in the oxide-precursor material to produce phase-pure zirconium-based mononitrides. To further determine the precise solubility limit of erbium (or other REE) in ZrN, electron microprobe analysis (EPMA) will be performed on a polished surface to determine the phase diagram.

Figure 6: Carbothermic Reduction / Nitridization of Zr$_{1-x}$Er$_x$O$_{2x/3}$. After 20 h at 1700°C the nitridization was completed and the formation of Zr$_{1-x}$Er$_x$N (lattice parameter $a = 4.6085(3)$ Å) and (Zr$_{1-x}$Er$_x$)$_2$(N,O)$_3$ (lattice parameter $a = 10.940(1)$ Å) was observed.