

Task 28

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

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BACKGROUND

Synthesis of actinium mononitrides using carbothermic reduction of the corresponding oxides has a few outstanding issues, including the formation of secondary phases such as oxides and carbides and low densities of the final product. Furthermore the requirement of a high process temperature at 1700°C, for more than 12 hours is also a drawback particularly for Americium-bearing samples. Therefore, it is important to explore the use of other possible routes to synthesize actinide mononitrides.

A low temperature process is used in this research to produce actinide mononitrides using a fluoride route in which the first step is to mix the actinide oxide with NH_4HF_2 . The second step involves the heat-treatment of the resulting ammonium actinide fluoride salts in ammonia atmosphere. Using different analytical techniques available, the experimental conditions can be studied and optimized to synthesize the required materials with high phase purity. Such available techniques are X-ray Powder Diffraction (XRD), Thermogravimetry and Differential Scanning Calorimetry (TG/DSC), and microscopic techniques such as Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Once the experimental conditions are studied and optimized, a number of actinide nitride systems (uranium, thorium, and neptunium) will be synthesized and characterized to provide knowledge on the chemistry of the systems. Characterization of these nitride systems will include chemical phase identification, lattice parameter refinements, morphological studies, microstructural verifications, thermal behavior, reaction mechanism, and reaction kinetics.

RESEARCH OBJECTIVES AND METHODS

The research objectives are:

- To explore a low-temperature fluoride route to synthesize actinide nitrides.
- To characterize actinide nitrides structurally and thermally.

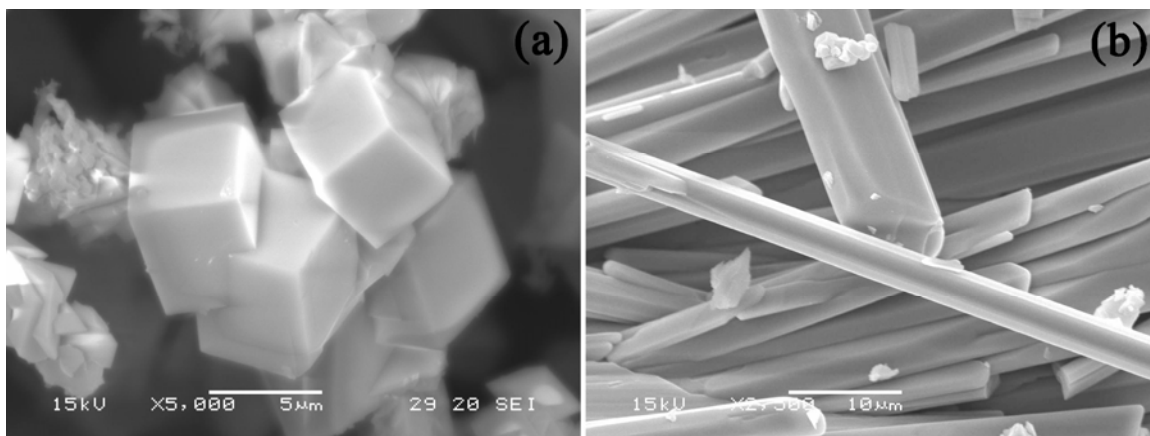
- To use high resolution TEM techniques to explore the microstructure of the radioactive samples.

RESEARCH ACCOMPLISHMENTS

Uranium based nitride synthesis and characterization

The fluoride route was successfully used to synthesize three uranium nitride samples with different stoichiometry (UN_2 , U_2N_3 , and UN). Experimental conditions were optimized to synthesize high phase purity UN (97 wt.%). Thermal decomposition of UN_2 under different atmospheric conditions was also studied, and ultra high purity argon could successfully be used to reduce the sample completely to UN at 1100°C, see graph on the opposite page. UN_2 and U_2N_3 decomposition kinetics into UN were studied under argon at three different temperatures (1000, 1050, and 1100°C).

Optical microscopy and SEM were used to explore the morphology of uranium nitride samples. Bright Field Transmission Electron Microscopy was also used to confirm the morphological observations. Microstructural studies of the samples were carried out using high resolution (HR) TEM with the help of selected area diffraction (SAD) patterns. X-ray energy dispersive spectrometry of TEM was utilized to characterize the elemental distribution and to verify the phase purity of the samples. Powder XRD patterns of the as-synthesized uranium nitrides, UN_2 , U_2N_3 , and UN were collected and analyzed. Optical microscopic studies showed that the particle sizes of these uranium nitride samples range from 100 to 5000 nm. The microstructure of the UN sample shows the presence of UO_2 as a secondary phase on the surface of the sample. In this region, the lattice fringes correspond to the (222) interplanar d -spacing of UO_2 . X-ray Energy Dispersive Spectrometry (XEDS) demonstrated that U was prominent, but it is difficult to identify the presence of N due to overlaps with peaks from O and C. However, the magnified XEDS spectra verifies the presence of N in samples, and this figure also displays the presence of O only in the UN sample. Thus, the XEDS verifies the phase purity of the



Scanning Electron Microscopic images of the (a) $7\text{NH}_4\text{F} \cdot 6\text{UF}_4$ and (b) $(\text{NH}_4)_4\text{ThF}_8$ samples. (a) $7\text{NH}_4\text{F} \cdot 6\text{UF}_4$ particles are well-crystallized (hexagonal unit cell with a rhomb-centered, a (b) = 15.40 Å and c = 10.49 Å and UN_2 is cubic (fcc) with a = 5.310 Å) (b) Well-crystallized $(\text{NH}_4)_4\text{ThF}_8$ acicular-shaped particles (triclinic unit cell with lattice parameters a = 8.477, b = 8.364, and c = 7.308 Å).

synthesized sample.

Thorium based nitride synthesis and characterization

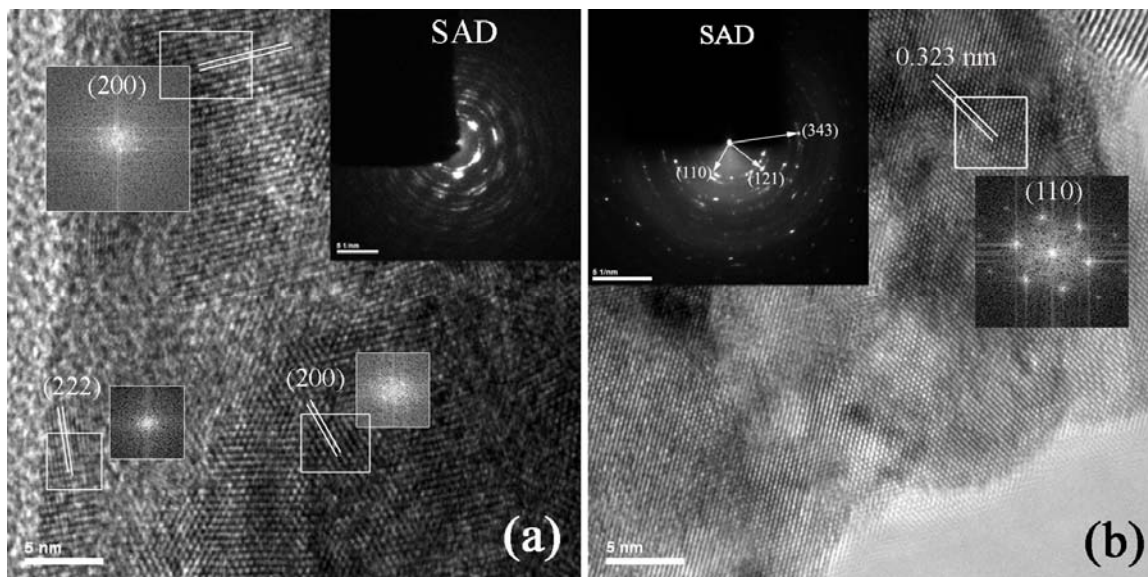
Use of the fluoride route was successful only up to the formation of ThNF. The removal of fluorine, which should have led to the formation of thorium nitrides was unsuccessful at different experimental conditions. However, the characterization of ammonium thorium fluoride and ThNF was done using the above mentioned techniques.

Other progress

- $(\text{NH}_4)_4\text{NpF}_8$ was found to be formed at room temperature for the reaction of NpO_2 with NH_4HF_2 after two days.
- Polycrystallinity of $(\text{NH}_4)_2\text{NpF}_6$ could be explained by observing the nanostructure of the compound by high-resolution transmission electron microscopy.
- Amorphous characteristics and disturbances in the lattice fringe formation were seen in the nanostructure of $(\text{NH}_4)_2\text{NpF}_6$.
- First NpN sample was synthesized by heating $(\text{NH}_4)_4\text{NpF}_8$ under NH_3 and subsequently under argon.
- The NpN sample was gold/yellow color. A secondary NpO_2 phase was also observed in the sample. DFT calculations of the thermodynamics properties of NpN.

ACADEMIC YEAR HIGHLIGHTS

- ◆ Low temperature synthesis of Np nitride (NpN) confirmed June 2008. First transuranic synthesis of the nitride at UNLV.
- ◆ G.W.C. Silva, C.B. Yeaman, L. Ma, G.S. Cerefice, K.R. Czerwinski, and A.P. Sattelberger, "Microscopic Characterization of Uranium Nitrides Synthesized by Oxidative Ammonolysis of Uranium Tetrafluoride," *Chem. Mater.*, 20(9), 3076-3084, 2008.
- ◆ G.W.C. Silva, F. Poineau, A. Sattelberger, and K.R. Czerwinski, "Low-temperature fluoride route for actinide ceramic synthesis," European Research Materials Society, Strasbourg, France, May 2008.
- ◆ P.F. Weck, E. Kim, N. Balakrishnan, F. Poineau, C.B. Yeaman, and K.R. Czerwinski, "First-principles study of single-crystal uranium mono- and dinitride," *Chemical Physics Letters*, 443(1-3), 82-86, 2007.
- ◆ G.W.C. Silva, C.B. Yeaman, G.S. Cerefice, F. Poineau, and K. Czerwinski, "Evaluation of a low temperature fluoride route to synthesize actinide mononitrides," 234th ACS National Meeting, Boston, MA, August 2007.
- ◆ C. Silva, T. Sullens, P. Weck, F. Poineau, T. Hartmann, C. Yeaman, A. Sattelberger, G. Jarvinen, D. Clark, and K. Czerwinski, "Novel Routes for the Synthesis of Actinide Nitrides," ACE Workshop on AFCI Materials, Idaho State University, Boise, ID, May 2007.



High resolution TEM images of (a) UN and (b) ThNF samples. (a) Crystallography of UN was confirmed using the lattice fringes of HRTEM image, and the secondary oxide phase was only identified at the surface of the particle edge. (b) ThNF crystal structure which is determined using XRD was confirmed by the HRTEM and SAD pattern.

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