2007

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

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Task 28
Impact of the Synthesis Process on Structure Properties for AFCI Fuel Candidates
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BACKGROUND
Synthesis of actinium mononitrdes 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 mononitrdes.

A low temperature process is used in this research to produce actinide mononitrdes using a fluoride route in which the first step is to mix the actinide oxide with NH4HF2. 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 (UN2, U3N5, and UN). Experimental conditions were optimized to synthesize high phase purity UN (97 wt.%). Thermal decomposition of UN2 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. UN2 and U3N5 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, UN2, U3N5, 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 UO2 as a secondary phase on the surface of the sample. In this region, the lattice fringes correspond to the (222) interplanar d-spacing of UO2. X-ray Energy Dispersive

Scanning Electron Microscopic images of the (a)7NH4F.6UF4 and (b) (NH4)4ThF8 samples. (a) 7NH4F.6UF4 particles are well-crystallized (hexagonal unit cell with a rhomb-centered, a (b) = 15.40 Å and c = 10.49 Å and UN2 is cubic (fcc) with a = 5.310 Å) (b) Well-crystallized (NH4)4ThF8 acicular-shaped particles (triclinic unit cell with lattice parameters a = 8.477, b = 8.364, and c = 7.308 Å).
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 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 lead 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.

![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.](image)

**Pseudo-first-order kinetics of UN2 denitridding at 1100°C.**

\[ k = 0.076172 \text{ (18355)} \text{ min}^{-1} \]

**FUTURE WORK**
- Explore other experimental conditions and chemicals to synthesize thorium nitrides.
- Study any reaction mechanism and kinetics involved in thorium nitride formations.
- Characterize thorium-based nitrides using the above mentioned techniques.
- Determine the ammonium bifluoride reaction with neptunium oxide.
- Explore the reaction route to synthesize Np-based nitrides.

**ACADEMIC YEAR HIGHLIGHTS**