Contract No:

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Disclaimer:

Title: 3D Characterization of Microparticulates

The internal chemical and structural properties of particulates produced from nuclear processes may hold signatory information regarding formation mechanisms (both chemical and nuclear). Instruments and techniques capable of internal particulate characterization have only recently become available within the past decade. Such techniques include electron backscatter diffraction (EBSD), transmission kikuchi diffraction (TKD), and high resolution transmission electron microscopy (HRTEM). This effort sought to demonstrate these techniques on commercially available materials as a proof of concept. Samples were transported to Clemson University for the advanced 3D capable preparation method of ion beam milling which can remove surrounding material from a feature of interest and section a particulate revealing the internal microstructure. Once thinned, the particles were analyzed with HRTEM; with TKD and EBSD analysis queued. During the method exercise several technical advances were made including: determination of preferred substrates, testing of particle relocation algorithms, successful demonstration of methods on particles 1-2 microns in diameter, and measurement of internal structure via HRTEM. Further efforts may include testing of different uranium compounds and testing of EBSD/TKD capabilities.

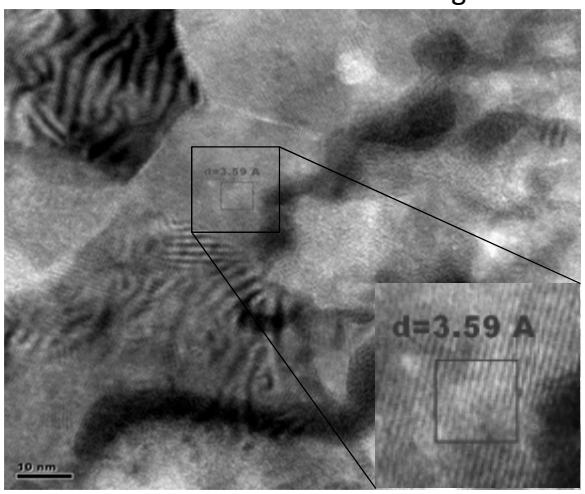

Figure: High Resolution HRTEM image of UF_4 particle with lattice fringes consistent with known structure.

Awards and Recognition

The director of the Clemson Microscopy Center, Dr. Saraf Laxmikant, has expressed repeated interest in continued efforts in uranium analyses with advanced microanalytical methods, including emails and discussions with SRNL senior management.

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature **Date**

3D Characterization of Microparticulates

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Subcontractor: S. Laxmikant; T. Darroudi (Clemson)

Thrust Area: ST3

Project Type: Exploratory

Project Start Date: Jun 1, 2015
Project End Date: September 30, 2015

The internal chemical and structural properties of particulates produced from nuclear processes may hold signatory information regarding formation mechanisms (both chemical and nuclear) and duration within the environment. Instruments and techniques capable of internal particulate characterization have only recently become available within the past decade. Such techniques include electron backscatter diffraction (EBSD), transmission kikuchi diffraction (TKD), and high resolution transmission electron microscopy (HRTEM). This effort sought to demonstrate these techniques on commercially available materials as of proof of concept. Particles were pre-selected for initial scoping studies at SRNL and were either uranium tetrafluoride or uranyl oxalate. Samples were transported to Clemson University for the advanced 3D capable preparation method of ion beam milling which can remove surrounding material from a feature of interest and section a particulate revealing the internal microstructure. Once thinned, the particles were analyzed with HRTEM, with TKD and EBSD analysis queued. During the method exercise several technical advances were made including: determination of preferred substrates, testing of particle relocation algorithms, successful demonstration of methods on particles 1-2 microns in diameter, and measurement of internal structure via HRTEM. Further efforts may include testing of different uranium compounds and testing of EBSD/TKD capabilities..

FY2015 Objectives

- Demonstration of correlated 3D electron microscopy methods on uranium-bearing particles
- Determination of technical challenges for this type of characterization, including EDS/EBSD spatial resolution, TKD, phase ID quality, and specimen material properties' requirements (i.e. organic/inorganic)

Introduction

The internal structure of a particulate material from a chemical or nuclear process can hold details on signatory information regarding their formation and duration in the environment, particularly when complemented with other methods such as isotopic measurements and/or Raman spectroscopy. To date no published efforts exist on characterization of such particulate materials with 3D techniques, but with utilization of electron microscopy techniques such as electron backscatter diffraction (EBSD)[1] and energy dispersive spectroscopy (EDS), 3D interrogation of crystalline/elemental structure is possible with nanometer resolution. Correlative microscopy is required as not all of these analysis may be conducted within a single instrument; a coordinate system using fiducial marks

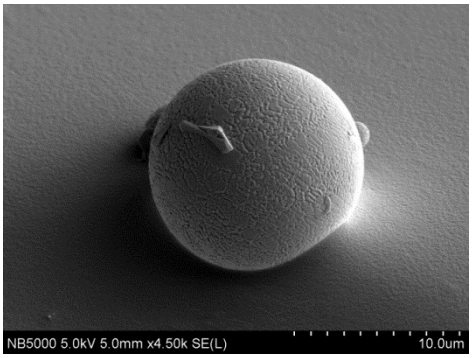

Figure 1. UF_4 particle secondary electron ion image; coated with Pt prior to ion beam milling.

allows for a particle to be relocated when switching between instruments for re-analysis.[2]

This effort focused on testing instrument capabilities and testing advanced microanalytical methods at Clemson University for the internal structural characterization of materials of interest, such as UF_4 as shown in Figure 1. The Clemson University Microscopy Center was chosen because of their state of the art instrumentation and expertise in microanalysis and associated techniques. The scope of this study was proof of concept, with particles being produced at SRNL or available as commercially available purchases, and transported to Clemson University Microscopy further preparation and microanalysis. The demonstrated work and concurrent method development has enhanced SRNL knowledge and capabilities for future work in particle analysis.

Approach

The general approach to demonstration of tools and methods is shown in Figure 2 and includes initial designation as a particle of interest, sample preparation, a cut out procedure, mounting/thinning, and final internal structural analysis. The particle generation took place at SRNL with a focus on using commercially available uranium samples. Two samples types were preselected (UF_4 and uranyl oxalate) do to their commercial availability or ease of synthesis. After an initial sample scoping study at SRNL to locate features of interest, logging their coordinates with fiducial marks, they were transported to

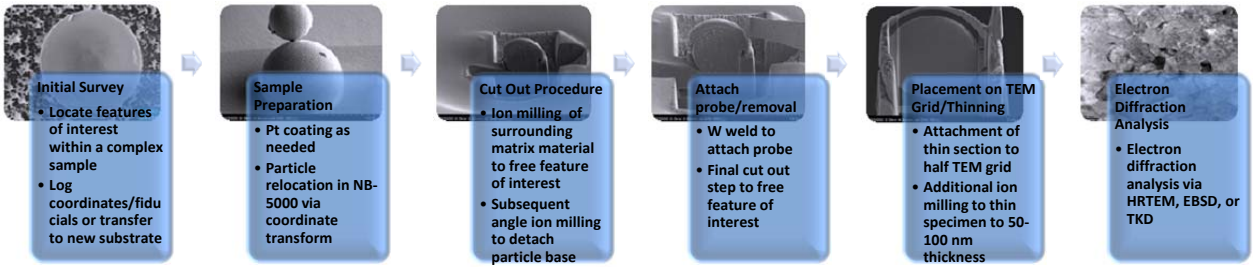

Figure 2. Illustration of the sequence of steps needed to locate particulates of interest and then processing required to render a specimen suitable for internal characterization.

Clemson microscopy center to cut out and remove the particles by ion milling. Subsequent thinning by focused ion beam (FIB) and attachment to a TEM half grid readied the specimen for further analysis. The milling exposes the particulates inner structure and arranges them in a more convenient geometry for electron backscatter diffraction and elemental characterization. This analysis can produce a "map" of both elemental and diffraction information correlated to the entire region of interest, potentially allowing unambiguous identification of the phases present (i.e. UO_2 versus U_3O_8), and additional identification of trace elements and general microcrystalline structure.

Results/Discussion

At first, particles from legacy samples on carbon tape were attempted as shown in Figure 3. However, this proved problematic when attempting to remove the particle with the focused ion beam (FIB) due to the number of collocated environmental microfeatures on the substrate and redeposition of the carbon substrate within the vicinity. The extra microfeatures congested the region of interest

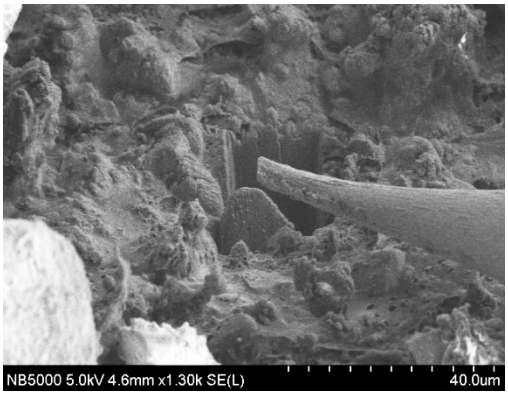

Figure 3. SEM image of particle slice still embedded in a carbon substrate; microprobe failed to contact particle due to surround matrix.

hindering attempts to cut beneath the particle for subsequent removal and attach the microprobe for extraction. Although this specimen failed, subsequent manual relocation of similar specimens in a SRNL laboratory under a light microscope, followed with physical removal onto a flat Si substrate solved these problems. Other particulates of interest (UF_4 and $UO_2(C_2O_4)\cdot xH_2O$) were directly placed on polished carbon or Si wafer substrates in the laboratory and when particle extraction was attempted, they were much more amenable to removal. Overall approximately ten particulates of UF_4 and $UO_2(C_2O_4)\cdot xH_2O$ were individually ion milled, extracted from the substrate, mounted on a TEM half grid, and analyzed with HRTEM to verify internal crystal structure. Unfortunately, neither TKD nor EBSD were attempted to temporary instrument outages.

Analysis by HRTEM x-ray diffraction was performed on UF_4 and uranyl oxalate, shown in Figure 4. HRTEM of crystalline materials results in lattice fringes or regions of a sample where the ordered atomic structure interacts with the electron beam to form parallel lines. The distance between these lines represents interatomic layer spacings (or d-spacing), which can be compared to known values, see tables 1. Comparison of values for uranyl oxalate shows several potential species with varying hydration states. The uranyl oxalate d-spacing correlates best to the anhydrous or monohydrate phase of uranyl oxalate reference by Bressat et al[3], with increased deviation from 0.07-0.08 Å difference from 3.18 Å as reported by Tel et al[4] for the trihydrate species. The d-spacing of UF_4 particles were in agreement with previous data from the ICDD database, with a difference of 0.03 Å. Other potential phases included a hydrated form of the material (not shown), but as material is stored in temperature and humidity controlled chambers, an unrelated work confirmed the pattern via XRD that the anhydrous assignment is most probable.

Chemical Species	Measured (Å)	Referenced (hkl) (Å)
$UO_2(C_2O_4)\cdot xH_2O$	3.11	3.18 (112,141)[1] Trihydrate 3.11 (-103)[2] Anhydrous 3.10 (023)[3] Monohydrate
UF_4	3.59	3.56 (221)[4] Anhydrous

Table 1. Comparison of reference data and measured data for uranyl oxalate and UF_4. 1)Referenced data reported by Tel et al.,[1] 2) Bressat et al. (PDF #00-020-1369), 3) Bressat et al. J. Ch. Phys. Tome **1964,** 64, 816, 4) Kern et al. (PDF #01-082-2317)

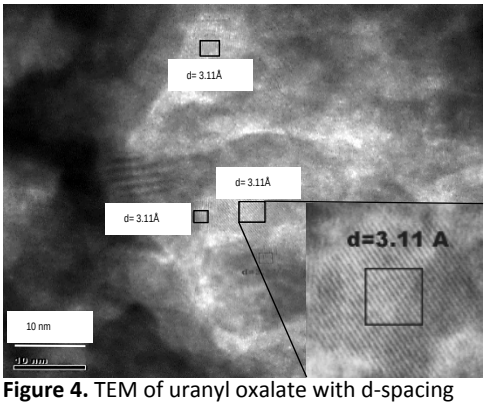

Figure 4. TEM of uranyl oxalate with d-spacing and blown up striations (inset).

TKD and EBSD has yet to be demonstrated on our particulate matter due to instrumentation challenges. When it is performed, this will answer unknown questions of the practical limits of detection of the technique, grain size, or sample robustness (i.e. resistance to electron beam damage). Regardless the existing work above provides proof that uranium particles can be characterized using advanced micro-analytical techniques. These experiments have also demonstrated a need to establish a documented workflow to ease future collaborative work with Clemson University.

FY2015 Accomplishments

- Transfer and relocation of particles of interest using a coordinate transfer system
- Demonstrated sample integrity survives milling and cut out procedures

- Established subcontract with Clemson University and utilized their state of the art instruments and microanalytical expertise
    - Successful execution of methods outlined in Figure 3
- Analysis of particles by HRTEM x-ray diffraction
    - Demonstrated repeatability measurements of different particulates for structural assignment

Future Directions

- Continued particle analysis of a broad range of uranium chemical species from commercial sources using HRTEM, TKD, and EBSD.
- Establish a documented workflow to ease future collaborative work with Clemson
- Inclusion of scoping results into new proposals and existing projects for specific nuclear material particulates

FY 2015 Publications/Presentations

A subset of this effort focused on UF_4 chemical characterization has been included in a forthcoming publication: Villa-Aleman, E.; Wellons, M. "Characterization of Uranium Tetrafluoride (UF_4) with Raman Spectroscopy", *Journal of Raman Spectroscopy,* submitted 2015.

References

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(2) Admon, U.; Donohue, D.; Aigner, H.; Tamborini, G.; Bildstein, O.; Betti, M. *Microscopy and Microanalysis* **2005**, *11*, 354.

(3) Bressat, R., Claudel, B., Trambouze, Y. *Journal de Chimie Physique et de Physico-Chimie Biologique* **1964**, *61*, 816.

(4) Tel, H., Bulbul, M., Eral, M., Altas, Y. *Journal of Nuclear Materials* **1999**, *275*, 146.

Acronyms

EBSD – Electron backscatter diffraction
EDS – Energy Dispersive Spectroscopy
EM – Electron Microscopy
FIB – Focused Ion Beam
HRTEM – High Resolution Transmission Electron Microscopy
ICDD – International Centre for Diffraction Data
SRNL – Savannah River National Laboratory
TEM – Transmission Electron Microscopy
TKD – Transmission Kikuchi Diffraction

Intellectual Property

None

Total Number of Post-Doctoral Researchers

One postdoctoral researcher worked on the project: Michael DeVore II