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Electron energy loss spectroscopy investigation through a nano ablated uranium dioxide sample

Claude Degueldre [a,*], Robin Schaeublin [b], Julijana Krbanjevic [b], Eugenia Minikus [b]

[a] NES, Paul Scherrer Institut, 5232 Villigen, Switzerland
[b] CRPP, EPFL, 5232 Villigen, Switzerland

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ABSTRACT

A lamella of uranium dioxide ($\sim 10 \times \sim 10 \times \sim 0.02$–$0.20$ μm) was produced by focused ion beam for transmission electron and electron energy loss spectroscopy (EELS) examinations. This sample allows quantitative analysis of the EEL spectra recorded for UO_2 as a function of the thickness. The M, N, O and P edges were recorded over zero loss to 4000 eV loss. The edges allow reconstruction of the electronic transitions, the lowest energy loss edges for P transitions corresponds to P3 electron transition (17.2 eV) from U6p3/2 level. The edge analysis allows also better interpretation of the loss spectrum with identification of the plasmon peak of the core electron transition edges. In addition, the energy lost was studied through a range of thicknesses going from ~20 to ~200 nm to derive the electron mean free path and cross section for inelastic scattering in the plasmon part of the spectrum. The mean free path of inelastic electron for uranium dioxide is compared with that reported earlier for other oxides from Be to Bi and for 200 keV incidents electrons. The present study emphasises the potential of combining FIB and EELS for the analysis of actinide compounds.

1. Introduction

Transmission electron microscopy (TEM) has been used for decades to characterize actinide materials [1], in particular uranium dioxide. Uranium exhibits several valence states and the reduction of U(VI) and U(V) species by electrons in nanometer powders of uranium oxide was addressed in the studies of UO_2 oxidation [2]. This original method makes it possible to synthesize by reduction under anoxic conditions nanometer UO_2 powders with a calibrated size. The powder characterization by X-ray diffraction, X-ray photoelectron spectroscopy and TEM shows the formation of spherical crystallites of UO_{2+x} of about 5 nm in size.

Single crystals of uranium dioxide, deformed under compression up to embrittlement, were examined by TEM [3]. They revealed dislocation structures consisting of numerous dipoles and dipolar loops. Particular features were noted in the dislocation arrangements which can be related to several of the theories of dipole formation. It has also been analysed using electron energy loss spectroscopy (EELS) [4]. In another study, corroded spent uranium oxide fuel showed in TEM and EELS enriched region contained U, Am, Ru, Zr and minor amounts of rare earth elements [5]. Precipitated uranium oxide phases identified as U_3O_8 were characterized by EELS using M (e.g., 3d→5f) and N (e.g., 4d→5f) edges recorded for the nano-crystals, between U(VI) secondary phases and the corrosion surface. These authors use the M_5/M_4 ratio to estimate the redox of U in the oxides.

Another work reports an EELS analysis from phase-specific regions of U metal and UO_2 [6]. The $N_{4,5}$ (i.e., 4d→5f) spectra were analyzed using the spin–orbit sum rule. The results show that the technique is sensitive enough to detect changes in the branching ratio of the white-line peaks between the metal and dioxide of uranium. The data suggest that the metal–oxide bonds in UO_2 are strongly covalent in nature and do not exhibit an integer valence change as would be expected from purely ionic bonding.

Core-loss EELS results suggest that tetravalent uranium compounds have an energy loss resolvable from hexavalent compounds. Indeed, as shown in e.g., [7], shoulders of the uranium $O_{4,5}$ edge (e.g., 5d→5f) allows distinguishing UO_2 from UF_4. In the presence of carbon, correction techniques must be applied. However, low-loss spectrum characteristics allow distinguishing the carbon from a holey substrate from the uranium oxide specimens. Uranium oxides, fluorides, and minerals show a tendency of reduction of uranium toward 4+ under the electron beam. The conditions for low-loss analysis need to be as vigorous as those for core losses. They need to be done without altering the valence of most oxides. From a systematic investigation point of view it must be noted that the uranium P_{1-3} transitions were however never reported by EELS.

The connection between the experimentally observed electron energy loss spectra and elevated temperature scanning tunneling images of surfaces of semiconducting uranium dioxide UO_2 was

* Corresponding author. Tel.: +41 56 310 41 76.
E-mail address: claude.degueldre@psi.ch (C. Degueldre).

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also analysed [8]. The combination of electron energy loss spectroscopy, atomic-resolution tunneling imaging and first-principles *ab initio* calculations was shown to provide a powerful tool for studying electronic and structural properties of surfaces of actinide oxides. EELS can consequently provide information on the structure of UO_2 that can be precious for the analyses of the thermal conductivity in terms of lattice, radiation and electronic components such as recommended [9].

The actinide compound samples for EELS investigation in the TEM (mainly at low energy) require careful preparation such as that provided by focused ion beam (FIB). This technique is based on deposition and ablation of materials. FIB systems operate in a similar fashion to a scanning electron microscope (SEM) except that it uses a finely focused beam of ions (usually gallium). It can be operated at low beam currents for imaging or high beam currents for site specific sputtering or milling. Since about 10 years FIB is widely used routinely for the preparation of electron transparent thin specimens, adequate for TEM investigations.

However, it should be noted that FIB development started more than 40 years ago and was applied for sputtering and thin film deposition in few laboratories. In the late 1970s two FIB sputtering units were used in CEA for preparing actinide targets [10]. Both were mounted in glove boxes. One apparatus was used for low specific activities, i.e., Th and U isotopes and the other for high specific activities, i.e., Pu and trans-Pu isotopes. Both were used for metals, oxides or other chemical forms of actinide deposits as thin films. Further sputtering work was carried out at CEA in the 1980s [11]. Targets were prepared for very precise specifications. These thin film deposits were made of actinides from Th to Cf. In the US, thin film production of 'alpha emitters' samples were also performed in the 1980s. Again ion beam sputtering was utilised for the preparation of thin films used as targets. Work was carried out in the Isotope Research Materials Laboratory at ORNL [12] to prepare actinide targets up to 100 $\mu g\ cm^{-2}$ by ion beam sputtering and thin film deposition.

More recently at AWE [13], FIB was required for site specific TEM sample extraction to examine using electron spectroscopy the composition and surface structure of uranium welded by an electron beam. Surface composition to a depth of a few microns was determined using SIMS profiling, and direct thickness measurements of surface over-layers on the metal were made using FIB. Here the material was cleaned up by FIB abrasion; no micro-samples were however produced by FIB.

In the present work, uranium dioxide was investigated by EELS in order to determine the valence state of uranium for a better understanding of its electronic structure in the redox state. Specimens were extracted by FIB. The EELS data produced in this study would never be gained without the high quality of the samples produced by FIB. Requirement of FIB samples are a well defined geometry and quality, i.e., contamination free.

2. Experimental and data treatment

The investigated sample was a UO_2 polycrystalline piece. The sample preparation by FIB, the TEM observations and EELS measurements were done at the electron microscopy laboratory (EML) at PSI. The EML was recently upgraded under the initiative of the author for handling of alpha isotope material with an activity below 100 LA (limit of autorisation) corresponding to a C-Lab, allowing the work on small actinide sources.

2.1. Focused ion beam

The FIB work was carried out with a Zeiss Nvision 40 Cross-beam workstation. It includes both a focused ion beam and a scanning electron microscope. The FIB unit operates with a source of Ga^+ ions that can be accelerated from 1 to 30 kV; the SEM unit operates from 0.5 to 30 kV. The FIB resolution reaches 4 nm for 30 kV and 1.6 nm for the SEM at 30 kV. The minimum usable Ga^+ ion beam size is 4 nm. The unit is completed with an Oxford Instruments energy-dispersive spectrometer (X-ray EDS) unit for elemental analysis. The instrument includes: a chamber SE detector, an Inlens EsB detector, an Inlens SE detector, a STEM detector, a 4Q BSD detector, and a cryo stage from Gatan.

2.2. Transmission electron microscopy and electron energy loss spectroscopy

The transmission electron microscope is a JEOL 2010 type TEM unit equipped with a LaB_6 electron gun and operated at 200 keV. The TEM point to point resolution is 2.3 Å. The TEM unit is equipped with a Gatan Enfina electron energy loss spectrometer. The EELS energy resolution was 0.5–1.0 eV in the studied domain. EEL spectra images were taken by Gatan Orius 11Mpixels CCD camera.

The EELS data were acquired and worked out using Gatan's EELS analysis tools included in Gatan DigitalMicrograph software. The analysis routines follow, wherever possible, a similar (or often identical) approach to that adopted in EL/P. Continuing the underlying philosophy of EL/P, the EELS analysis routines encapsulate many details in a few high-level commands. For instance, once a spectrum from 0 to about 500 eV, including the zero loss peak (ZLP) has been acquired, the menu 'thickness measurement' in DigitalMicrograph® may be used to evaluate the local sample thickness with a precision of 10%.

3. Results

3.1. Sample preparation by focused ion beam

The piece of uranium dioxide is a sample of non-irradiated fuel (UO_2) material. The sample has a tier like shape with sizes around 1.9 mm, 2.3 mm and 2.2 mm for the arc of 57°. The thickness of the tier was 0.25 mm. Its total activity does not exceed 0.9 LE (limit of exemption). The sample was glued with C glue on a typical SEM Al stub. The sample was first examined using the SEM instrument of the NVision 40. The trapezoidal machining of the sample necessary for the extraction of the thin lamella was carried out using 30 kV accelerated Ga^+ ions. For a current of 30 nA, 10 μm were eroded in 14 min, corresponding to an ablation rate of $\sim 10\ nm\ s^{-1}$, which is fast compared to light element material erosion (e.g., SiO_2 or $Si_4Al_2O_{11}$). The coarse lamella, about 1 μm thick, now liberated on 3 sides was subsequently freed from below using lateral–diagonal ion milling.

Once the coarse sample was prepared, the transfer needle was approached and attached using carbon strip produced by deposition of carbon from a precursor gas decomposed by the ion beam. This allowed fixing the sample in order to proceed to its complete liberation by ablation of the 4th side. The coarse lamella was subsequently lifted and approached to the TEM sample carrier made of a 3 mm half moon holding a comb like structure, the so-called 'omniprobe grid'. The specimen is fixed by carbon coating to one of the comb teeth. It was then freed from the transfer needle by sputtering away the carbon strip on the needle side.

The attached TEM lamella was then shaped to an edged lamella with variable thickness, allowing for the study of the thickness dependence of the EELS signal. For the fine milling to the final polishing, the ablation was carried out with a 2 kV Ga^+ ion current of 80 pA and with an incident angle from 30° to 1°. The TEM lamella sample was a $10 \times 10 \times (0.030–0.300)$ μm surrounded by