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Uranium trioxide behavior during electron energy loss spectroscopy analysis

Claude Degueldre [a,b,*], Evgeny V. Alekseev [c,d]

[a] NES, Paul Scherrer Institute, 5232 Villigen, Switzerland
[b] Département de chimie analytique, Université de Genève, Switzerland
[c] IEK6, Forschungszentrum Jülic, 52428 Jülich, Germany
[d] Institute für Kristallographie, RWTH Aachen University, Germany

HIGHLIGHTS

- EEL spectra recorded as a function of UO_3 sample thickness.
- The analysis was performed for the *P* and *O* edges.
- Reduction of UO_3 into U_4O_9 and/or UO_2 readily observed during TEM investigations.
- Reduction of UO_3 was confirmed by electron diffraction.

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ABSTRACT

A sample of uranium trioxide (UO_3) was produced by focused ion beam ($\sim 10\ \mu m \times \sim 10\ \mu m \times < 0.5\ \mu m$) for transmission electron and electron energy loss (EEL) spectroscopy examinations in a transmission electron microscope (TEM). The EEL spectra were recorded as a function of the thickness for the *P* and *O* edges in the low energy range 0–350 eV and were compared to spectra of UO_3 small grains attached to a TEM grid. The EEL spectrum was studied through a range of thicknesses going from ~60 to ~260 nm. The EEL spectra recorded for UO_3 are compared with those recorded for UO_2. The reduction of UO_3 into U_4O_9 and/or UO_2 is readily observed apparently during the TEM investigations and as confirmed by electron diffraction (eD). This redox effect is similar to that known for other redox sensitive oxides. Recommendations are suggested to avoid sample decomposition.

1. Introduction

Uranium dioxide is the most used compound in the nuclear industry e.g. Degueldre et al. (2011), however, several stable binary uranium oxides of such as U_4O_9, U_3O_8 and UO_3 are also found together with several meta-stable oxides between U_4O_9 and U_3O_8, (Hoekstra and Siegel, 1961). Uranium trioxide is the end member of the UO_{2+X} series. It may be found in the fuel production processes and spent fuel environment, however, it can significantly react with water and be reduced as described below.

The chemical reactivity of uranium trioxide (UO_3) with regards to water vapor is well known (Dell and Wheeler, 1963; Hoekstra and Siegel, 1973). The trioxide yields various forms of hydrates that can be formed from 20 to 100 °C. The uranium trioxide can be regenerated by dehydration of the hydrates at temperatures < 500 °C. The formation of UO_2 requires reduction or decomposition at temperatures > 500 °C.

In the nuclear fuel cycle UO_2 is prepared by the reduction of UO_3 under partial H_2 atmosphere up to 800 °C. Uranyl nitrate hexahydrate (UNH) or ammonium diuranate (ADU) are used as starting materials to obtain UO_2.

The preparations and characterization of five crystalline polymorphs of UO_3 ($\alpha, \beta, \gamma, \delta, \zeta$) as well as of amorphous UO_3 and $UO_{2.9}$ were already described in detail in the 60s (Wheeler et al., 1964). A detailed X-ray diffraction (XRD) study was made of phases formed during the thermal decomposition of amorphous and β-UO_3.

The analysis of UO_3 is reported in environmental science.

In Kosovo, a depleted-uranium penetrator, shot in 1999, collected in 2001, showed evident alterations including black and yellow coatings (Mellini and Riccobono, 2005). XRD indicated that the black coating mostly consists of UO_2, with possible presence of

* Corresponding author at: NES, Paul Scherrer Institute, 5232 Villigen, Switzerland.
E-mail address: claude.degueldre@psi.ch (C. Degueldre).

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other more oxidized uranium forms. The yellow material is mostly amorphous, with variable weak diffraction lines, due to minor embedded uraninite grains, or possibly to schoepite, $UO_3 \cdot 2H_2O$. A combination of synchrotron radiation based X-ray microscopic techniques applied on single depleted uranium (DU) particles has also been employed to characterise DU site-specific particles. The oxidation states and crystallographic forms of U in DU particles have been determined for individual particles isolated from selected samples collected at different sites in Kosovo and Kuwait contaminated by DU ammunition during the 1999 Balkan conflict and the 1991 Gulf war (Lind, et al., 2009). Presence of hydrated UO_3 was confirmed.

The combination of electron based analysis was also successfully used for the determination of the uranium valence state in the brannerite structure for example (Colella, et al., 2005). The inhomogeneous distribution of particulate uranium phases in the soil required however the development of methods to prepare transmission electron microscopy (TEM) thin sections (Buck, et al., 1995).

Uranium trioxide is also used as starting material for the synthesis of uranyl compounds. As an example UO_3 was recently used for the synthesis of uranyl molybdate UO_2MoO_4 (Suleimanov, et al., 2010) and more recently of uranium diphosphonates templated by interlayer organic amines (Nelson et al., 2013). The complex uranium oxide system was also recently reviewed for its relevance to catalysis (Idriss, 2010).

UO_2 was claimed (Rice, et al., 1999) to have an energy loss resolvable from UO_3. However, the electron dose required to achieve the transformation from 6+ to 4+ was more severe than that usually required to obtain satisfactory spectra. It was consequently noted that the possibility for reduction must be considered.

This paper focuses on a UO_3 and its stability during TEM/EELS analysis in the low energy domain (<200 eV) requiring short acquisition time (less irradiation effects). The study is completed by electron diffraction (eD) tests. The EELS results supposed to be gained for UO_3 are compared with those reported recently for specimen of UO_2 with various thicknesses (Degueldre et al., 2013).

2. Experimental

2.1. Material

The uranium trioxide was synthetized by thermolysis of hydrated uranyl nitrate. For preparation of UO_3 powder sample $(UO_2)(NO_3)_2 \cdot 6H_2O$ was used as a starting material. It was placed in Pt crucible and heated up to 420 °C in air atmosphere. The crucible was kept in a furnace for 6 h. The resulting material was a red powder which changed its color to yellowish–orange after 48 h. The material may react with the water in air producing the hydrated form of uranium trioxide. Consequently all operation and storage were carried out when possible under dry argon.

The sample preparation by FIB, the TEM observations and EELS measurements were carried out at the electron microscopy facility (EMF) at PSI. The EMF was recently upgraded for handling of alpha isotope material with an activity below 100 LA (limite d'autorisation) corresponding to a C-Lab, allowing the work on small actinide sources.

2.2. Focused ion beam

The FIB work was carried out with a Zeiss Nvision 40 Crossbeam workstation. It includes both a focus 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 (EDS) unit for elemental analysis.

2.3. 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. Electron diffraction (eD) was carried out in a standard manner with a fluorescent screen at a fixed distance L from the object. The diffraction pattern record is made with a digital camera. The TEM unit is also equipped with a Gatan Enfina electron energy loss spectrometer. The EELS energy resolution was 0.8–1.1 eV in the studied domain (but relative precision in the spectrum can be of the order of 0.1 eV). 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 EELS analysis routines encapsulate many details in a few high-level commands. For instance, once a spectrum from 0 to about 300 eV, including the zero loss peak (ZLP) has been acquired, the menu 'thickness measurement' in DigitalMicrograph® was used to evaluate the local sample thickness with a precision of 10%.

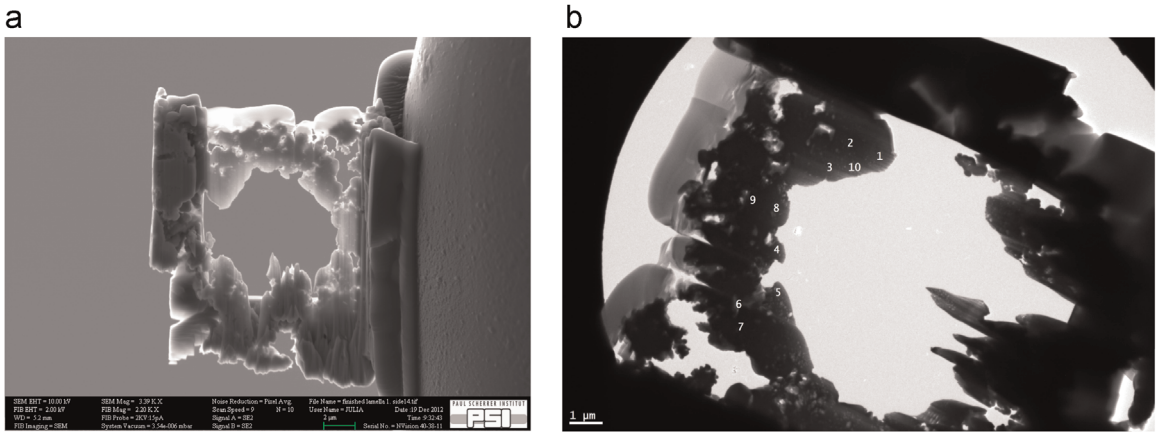

Fig. 1. (a) SEM of the UO_3 specimen as produced by FIB and (b) TEM micrographs of the FIB UO_3 sample prior EELS/eD investigations. Studied areas noted by numbers.