Oxidation of a depleted uranium-5 wt% molybdenum (U-5Mo) alloy in UHV by AES and XPS

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Funding information
EPSRC, Grant/Award Number: EP/G037388

Early stage oxidation of a dilute-depleted uranium-molybdenum alloy was analysed in situ under ultra-high vacuum conditions by AES and XPS. At the equivalent of less than 300 ns at 1-atm O2, U-5Mo oxidizes to form stoichiometric UO2. No molybdenum oxidation is observed. After an oxygen dose of approximately 39 L, the oxide layer approached a limiting thickness of approximately 2.4 nm. The oxidation kinetics followed a logarithmic rate law, with the best fit to the experimental data for the oxide thickness, \( d \), being given by \( d = 1.26 \log(0.12 + 0.56). \) Changes in oxygen KLL and 1s peak positions associated with transformation from chemisorbed oxygen to metal oxide were observed at similar oxygen doses of 2.3 and 2.6 L O2 by AES and XPS, respectively, which opens up the possibility of using well-characterized XPS chemical information to inform Auger peak shifts.

KEYWORDS
AES, corrosion, molybdenum, oxidation, uranium, XPS

1 | INTRODUCTION

The uranium-oxygen system exhibits one of the most complex chemistries for any metal. Thermodynamics predict the formation of numerous stoichiometries between UO2 and UO3. The study of this system has great significance since oxidation is a principal route to uranium corrosion. In atmospheric conditions, corrosion proceeds through a combination of reactions with oxygen and water vapour as described in Equations (1) and (2), respectively.3,4

\[
\begin{align*}
\text{U} + \text{O}_2 &\rightarrow \text{UO}_2 \\
\text{U} + 2\text{H}_2\text{O} &\rightarrow \text{UO}_2 + 2\text{H}_2
\end{align*}
\]

Uranium dioxide has a Pilling-Bedworth ratio close to 2, which describes the volume ratio between the oxide and underlying metal and is such that compressive stresses lead to defects in the oxide layer. This initially permits anionic diffusion to the metal surface, allowing further oxidation and ultimately cracking and spalling of the oxide. The oxide is therefore nonprotective and without any form of intervention; for example, in a change in storage conditions, full consumption of the metal will occur. For uranium, this poses significant safety concerns in terms of long-term storage and waste management, because the products are toxic, radioactive, and potentially pyrophoric if uranium hydride (UH3) forms.5

Depleted uranium (DU) has the isotopic fraction 0.2\% 235U and 99.8\% 238U and is a by-product of the processes that enrich the fissile fraction in natural uranium (0.7\% 235U and 99.2\% 238U) to useable levels in nuclear reactors. DU has many uses in its own right, such as aircraft counterweights, munitions, catalysis, radiation shielding, and reactor fuel applications, for example, re-enrichment, mixed oxide (MOX) production, or dilution of highly enriched uranium.6-9 However, because DU has similar chemical properties to natural and enriched uranium and, with lower 235U content, is less hazardous from a...
radiological perspective, it is also an attractive material for uranium research purposes.\(^7\)

Alloying is a common method for increasing the corrosion resistance of uranium, and range of elements has been utilized for this purpose, including Al, Mo, Nb, Ru, Si, Ti, V, Y, Zr, and V.\(^{10-13}\) Niobium is generally considered to be the most effective and has received considerable attention in the literature at various alloying amounts (2.5-14 wt%). XPS analysis has shown that increasing the Nb concentration from 2 to 8 wt% leads to a thinner oxide layer being formed.\(^{14}\) Scanning Kelvin probe force microscopy (SKPFM) and potentiodynamic polarization studies have shown that increasing the Nb concentration from 2.5 to 5.7 wt% improves corrosion performance.\(^{13}\)

In situ studies on U-Nb alloys at ultra-high vacuum (UHV) by XPS and AES found early stage oxidation to occur initially by the formation of UO\(_2\), followed by successively higher niobium oxides: NbO, NbO\(_2\), and Nb\(_2\)O\(_5\). It has further been proposed that a critical amount of Nb\(_2\)O\(_5\), specifically, is required to achieve enhanced corrosion protection based on providing a barrier to anionic diffusion.\(^{10}\) Similarly, a U-20 at% Zr was shown by XPS to form ZrO\(_2\) following 5 L* O\(_2\) dose, albeit to a lesser extent than uranium oxidation.\(^{17}\) Alloying with molybdenum has also been shown by gravimetric methods and X-ray diffraction (XRD) to improve corrosion performance compared with unalloyed uranium, however, not to the same level as for niobium.\(^{18-20}\) A recent XPS investigation into the effects of various surface preparation steps on the oxidation of a U-10 wt% Mo alloy found a protective role for molybdenum in the prevention of formation of higher uranium oxides, although this was following extended periods of exposure to 97% humidity.\(^{21}\)

To date, mechanistic studies that attempt to determine whether the initial process of U-Mo alloy corrosion exhibits similar characteristics to U-Nb alloys and whether any differences may have an effect on the lower protective performance of U-Mo are lacking. In this work, we use oxidation at extremely low-oxygen partial pressures (pO\(_2\) < 10\(^{-8}\) mbar) to study the very early stages of oxidation of the candidate U-5Mo alloy by AES and XPS.

### 2 | EXPERIMENTAL

#### 2.1 | Sample preparation

The sample was a 5 mm diameter disc of depleted uranium alloyed with molybdenum at 5 wt%. It was polished using increasingly fine grades of SiC abrasive paper down to P2500. The sample was rinsed and washed firstly with deionized water and then with isopropyl alcohol (IPA) prior to analyses.

#### 2.2 | Auger electron spectroscopy

AES was performed using a Thermo Scientific MICROLAB 350 scanning Auger microscope operating at a base pressure of 2.6 × 10\(^{-8}\) mbar (approximate pO\(_2\) = 5.20 × 10\(^{-9}\) mbar), employing a primary electron beam energy of 10 keV and a sample current of approximately 10 nA. Monoatomic argon-ion etching was performed immediately prior to analysis to remove the native oxide and expose the clean metal surface. Etching was performed with an EX05 argon-ion gun in a 2 × 2 mm raster pattern until the O KLL signal was no longer detectable. Auger spectra were collected over an energy range of 60 to 530 eV with a constant retard ratio of 4 and dwell time of 40 ms per 1.0 eV channel. The spectral scan parameters were determined following a period of method development to achieve a good compromise between speed of analysis, spectral information, and spectral resolution for the oxidation study. The time between the end of etching and start of the spectral scan was 8 seconds (0.03 L), and the analysis time of each iteration was 35 seconds (0.14 L). Auger spectra were collected in the direct mode and were taken up to an O\(_2\) dose of approximately 40 L (1 L = 10\(^{-6}\) Torr s) with 300 iterations.

#### 2.3 | X-ray photoelectron spectroscopy

XPS was performed using a Thermo Scientific Theta Probe photoelectron spectrometer operating at a base pressure of 6.6 × 10\(^{-9}\) mbar (approximate pO\(_2\) = 1.32 × 10\(^{-9}\) mbar) with a monochromated Al K\(_{\alpha}\) source (1486.6 eV). Again, monoatomic argon-ion etching was performed immediately prior to analysis to remove the native oxide and expose the clean metal surface. Etching was performed with an EX05 argon-ion gun in a 2 × 2 mm raster pattern until the O 1s signal was no longer detectable. High-resolution spectra were collected over appropriate energy ranges to record U 4f, Mo 3d, O 1s, and C 1s peaks with a pass energy of 50 eV and dwell time of 50 ms per 0.2 eV channel. Data were charge referenced to the O 1s peak for the purpose of comparing the UHV-formed oxide with the air-formed oxide. The time between end of etching and beginning of spectral acquisition was 23 seconds (0.02 L), and the analysis time of each iteration was 130 seconds (0.13 L). Spectra were taken up to an O\(_2\) dose of approximately 39 L with 300 iterations.

### 3 | RESULTS AND DISCUSSION

#### 3.1 | AES in situ UHV oxidation studies

Figure 1 presents AES spectra and shows oxidation progression from the clean metal surface, observed at 0.03 L O\(_2\), to detection of the O KLL peak at between 0.17 and 0.30 L O\(_2\) and the O KLL peak intensity starting to plateau beyond a dose of approximately 7 L O\(_2\). As shown in the inset graph for Figure 1, oxidation proceeded rapidly in the initial stages, but then, slowing towards a limiting oxide thickness was observed, as described by the Cabrera-Mott theory for thin-film growth.\(^{22}\) It was considered that the relatively unchanging O KLL intensity beyond 7 L O\(_2\) could result from the oxide growing to a thickness beyond the escape depth of Auger electrons; however, the XPS investigation (see §3.2) showed that this was not the case. Figure 2 shows an expansion of O KLL region for specific oxygen
exposures up to the approximate plateau point. The O KLL peak exhibited a slight shift of 1.5 eV after an approximate dose of 2.6 L O₂, which was attributed to initial chemisorption of oxygen species followed by transformation to oxygen within a solid metal oxide and is in agreement with similar work.¹⁶

For a similar range of oxygen exposures, Figure 3 shows an expansion of the 50 to 300 eV energy region containing the major uranium peaks. Since it was not possible to obtain a base vacuum of lower than 10⁻⁹ mbar in the AES instrument, speed of acquisition was favoured over spectral resolution, and pseudo-survey scans were used to cover the range of energies of interest rather than performing separate high-resolution scans. As a result, it was difficult to accurately resolve each individual uranium transition; however, a number of possible peaks were identified, as shown in the inset table in Figure 3. Assignments were made with the aid of a comprehensive Auger peak library designed specifically for this work, in which the theoretical Auger electron kinetic energy (E_{calc}) of all possible transitions for every element up to uranium in the periodic table (calculated using archival experimental data²³-²⁷) is available in a spreadsheet to be searched and referenced against observed peak positions (E_{obs}). All of the proposed uranium peaks were shown to shift to a lower kinetic energy with oxidation, indicating the potential for extracting chemical state information with Auger uranium studies. The main molybdenum peak (Mo MNN) at 190 eV was not resolved in the spectra because of the presence of the U N₆O₅O₄ peak with a similar kinetic energy. In order to provide additional chemical information and expand upon the AES results, the oxidation experiment was also carried out using XPS.

**FIGURE 1** AES spectra showing progressive in situ UHV oxidation for U-5 Mo, from bare metal through to an O₂ dose of 6.08 L. The inset graph plots O KLL peak intensity against O₂ dose up to approximately 15 L showing the change in the oxidation rate with O₂ dose. The U Auger peaks observed are specified in Figure 3.

**FIGURE 2** An expansion of the energy range 500 to 525 eV from the data in Figure 1 for a selection of O₂ doses. The O KLL peak was shown to shift by approximately 1.5 eV following an O₂ dose of approximately 2.6 L, as indicated by the dashed line.
3.2 | XPS in situ UHV oxidation studies

High-resolution spectra for U 4f, O 1s, and Mo 3d peaks at increasing oxygen exposures are shown in Figure 4. For the U 4f peak, the 4f7/2 and 4f5/2 peaks were initially observed at binding energies of 377.2 to 388.0 eV, respectively, corresponding the uranium metal. Upon oxidation, a second 4f peak doublet emerged with 4f7/2 at 380.8 eV and 4f5/2 at 391.6 eV, corresponding to the metal oxide. An O 1s peak was detected between 0.28 and 0.41 L O2, in agreement with AES data. The oxygen peak exhibited a slight shift of 1.4 eV after an O2 dose of 2.3 L, corresponding to the transformation of chemisorbed oxygen species to metal oxide species.

| Peak | Assignment | Ecalc (eV) | Eobs (eV) | Peak shift (ΔeV) |
|------|------------|------------|-----------|-----------------|
| 1    | O2P2V     | 73.4       | 74.4      | 1.4             |
| 2    | O2VV      | 86.2       | 91.0      | 4.4             |
| 3    | O2VV      | 94.8       | 97.3      | 2.9             |
| 4    | O2O2P2    | 107.2      | 107.1     | 2.8             |
| 5    | N2O2O5    | 184.4      | 187.9     | 3.4             |
| 6    | N2O3V     | 281.4      | 282.4     | 2.6             |

FIGURE 3 | An expansion of the energy range 60 to 300 eV from the data in Figure 1 for a selection of O2 doses. Six uranium peaks originating from O and N core shell electrons were observed. Dashed lines are used to highlight peak shifts as oxidation of the U-5Mo alloy surface occurred. The inset table provides initial peak energies from the bare metal surface (Eobs), the peak transition assignments, the calculated peak energies used to derive the assignments (Ecalc), and peak shift values (ΔeV), which are all to the lower kinetic energy side of the peaks in the pure metal spectrum.

FIGURE 4 | XPS U 4f, O 1s, and Mo 3d core level spectra showing progressive in situ UHV oxidation at a selection of O2 doses. Dashed lines show peak position shifts, or lack of, as oxidation progressed. Peak shifting in the U 4f doublet was characterized by the formation of separate oxide peaks at the higher binding energy side of the metallic peaks for both 4f7/2 and 4f5/2 components. The emergence of a satellite peak (SP) structure at higher binding energy was also observed for the 4f5/2 component as is commonly observed in uranium oxide spectra. It is likely that a satellite peak for the 4f7/2 component was obscured by the 4f5/2 metal peak. After an approximate O2 dose of 2.3 L, the O 1s peak exhibited a slight peak shift of approximately 1.4 eV to higher binding energy as chemisorbed oxygen species transformed to metal oxide species. The Mo 3d doublet peak exhibited no shift and was shown to reduce in intensity as the uranium oxide formed on the metal surface.
The Mo 3d peak is shown in Figure 4 as a function of oxygen dose. The doublet was observed at binding energies of 277.2 and 230.2 eV for 3d5/2 and 3d3/2, respectively, indicative of Mo in the metallic state. The peak did not exhibit a shift in binding energy, and the peak intensity decreased with increased O exposure, resulting from the growth of uranium oxide at the surface. The results demonstrate that molybdenum does not oxidize in the very early stages of oxidation of this alloy. At 38.5 L O2 in our XPS system, this is equivalent to approximately the first 270 ns in air (1 atm). Quantification by taking a Shirley background for Mo 3d and U 4f contributions of time zero spectra from three experimental repeats gave an average of 6.7 wt% Mo at the surface, which is marginally enriched compared with the nominal bulk amount, and a value of 4.8 wt% Mo as determined prior to the oxidation experiment by energy dispersive X-ray spectroscopy (EDS).

The lack of molybdenum oxidation at this stage is contrary to that of niobium when present as an alloying addition for uranium, which has been shown by XPS to oxidize after 10 L O2 in UHV conditions. This observation might be expected from a purely thermodynamic perspective. Table 1 lists Gibbs free-energy values for the formation of a selection of uranium, niobium, and molybdenum oxides. There is a substantially stronger thermodynamic driving force for niobium oxidation compared with molybdenum, especially for the critical oxide Nb2O5.

As shown in Figure 4, the main U 4f oxide peaks occurred at 380.8 and 391.6 eV for the 4f7/2 and 4f5/2 peaks, respectively, and did not shift throughout the analysis. This suggests that the composition of the oxide was invariant during the initial stages of oxidation. A significant amount of data exist in the literature regarding the XPS peak positions and peak shifts for different uranium oxide stoichiometries. Table 2 is a compilation of the available data and includes relevant values from this current work. Given the error values quoted in the various studies, which range from ±0.1 to ±0.3 eV, the most likely uranium oxide assignments, based on both the free energy of formation and binding energy considerations (Tables 1 and 2), are U3O8 and UO2. However, it is known that the presence of alloying elements can cause shifts in XPS peak positions and in a comprehensive review of XPS for determining uranium oxidation states by Ilton and Bagus, it was shown that the binding energies of the U4f1/2 peak were unreliable indicators of the chemical state based on structural and compositional factors.

Uranium oxides are typically accompanied by characteristic shake-up satellite peaks in the XPS spectra. In the same Ilton and Bagus review, it is suggested that the separation between satellite and primary peaks (ΔEs, p) is not so markedly influenced by oxide structure/composition and therefore a more reliable indicator of oxidation state. Unfortunately, satellite peak positions for oxides other than UO2 are not reported as commonly as the primary peak positions, and so, the number of pertinent citations is significantly less (Table 3). A number of groups assign the presence of a satellite peak at approximately 6.9 eV to the higher binding energy side of the 4f7/2 primary oxide peak to stoichiometric UO2,10,15,30-44 Allen et al describe the appearance of additional satellite structure at approximately 7.0 eV when UO2 is oxidized to superstoichiometric UO2+x. As shown in Figure 4, the only clear satellite peak observed for the UHV-grown oxide in this work was to the higher binding energy side of the 4f7/2 oxide peak and has a ΔEs, p value of approximately 7.0 eV. This is indicative of

### Table 1

| Compound | ΔG° | UO2  | UO8  | UO9  | NbO  | NbO2 | Nb2O5 | MoO2 | MoO3 |
|----------|-----|------|------|------|------|------|-------|------|------|
|          | 298 |      |      |      |      |      |       |      |      |
| UO2      | -1032 | -13370 | -4275 | -406 | -796 | -1900 | -533.0 | -668.0 |

Abbreviation: N/A, not applicable.

### Table 2

| Compound | U4f Binding Energy (eV) | U4f Peak Position | U4f Peak Shift | ΔE7/2 | ΔE5/2 |
|----------|-------------------------|-------------------|----------------|-------|-------|
| U metal  | 377.1<sup>29</sup>       | 387.8<sup>29</sup> | N/A            | N/A   |
| UO2      | 381.4<sup>40a</sup>      | 391.0<sup>40a</sup> | 3.0            | 3.2   |
| U3O8     | 381.2<sup>41a</sup>      | 391.2<sup>41a</sup> | 3.0            | 3.1   |
| UO3      | 380.6<sup>29</sup>       | 391.4<sup>29</sup> | 3.5            | 3.6   |

Abbreviation: U— as in the film, b— as a powder compared with observations from the current work.
As a continuation of the XPS experiment, the sample was removed from the instrument, air exposed for a period of 5 minutes in ambient conditions, and then reanalysed (for spectra, see online Supporting Information). The first point to note was broadening and shifting of the Mo 3d peaks associated with oxidation to MoO$_2$ and MoO$_3$. In addition, only the oxide component of the U 4f doublet remained, and clear satellite structures associated with the 4f$_{7/2}$ and 4f$_{5/2}$ oxide peaks were observed. The main oxide peaks appeared at 380.2 eV with $\Delta E_{\text{ox}} = 6.9$ eV for 4f$_{7/2}$ and 391.0 eV with $\Delta E_{\text{ox}} = 6.8$ eV for 4f$_{5/2}$. By consulting Tables 2 and 3, it is clear that the air-formed oxide was stoichiometric UO$_2$. Considering these peak positions relative to the main O 1s peak, it is interesting to note that the separation is exactly the same as that for the UHV-grown oxide relative to the corresponding main O 1s peak for both 4f$_{7/2}$ ($\Delta E_{\text{ox}} = 150.2$ eV) and 4f$_{5/2}$ ($\Delta E_{\text{ox}} = 139.4$ eV). This observation supports the conclusion that the UHV-grown oxide was also stoichiometric UO$_2$ and is in agreement with information in the literature concerning the diagnostic use of satellite peak positions instead of absolute core-level binding energies for determining uranium oxidation states.

### 3.3 Oxidation kinetics

Oxide thickness information was estimated from the XPS data, using the U 4f$_{7/2}$ oxide-to-metal peak ratio ($I_{\text{ox}}/I_{\text{m}}$) obtained by peak fitting and according to the relationship described in Equation (3), which assumes a uniform oxide layer, and was first described by Strohmeier.$^{45}$

$$d = \lambda_0 \sin \theta \ln \left[ \frac{N_{\text{ox}}I_{\text{ox}}}{N_{\text{m}}I_{\text{m}}} + 1 \right],$$

(3)

where $d$ is oxide thickness (in nm); $\lambda_0$ and $\lambda_m$ are the inelastic mean free paths (IMFPs) for the oxide and metal, respectively (in nm); $N_{\text{ox}}$ and $N_{\text{m}}$ are the volume densities of metal atoms in the oxide and metal, respectively; and $\sin \theta$ is the electron take-off angle relative to the sample surface.$^{45}$ IMFP values for the U4f$_{7/2}$ were determined from the TPP-2M equation as 1.8 and 2.9 nm for the metal and oxide, respectively.$^{54}$ The relative values for the Auger spectra are significantly smaller. Values calculated in the same manner for the U O$_2$P$_2$V are 0.5 nm for U metal and 0.7 nm for UO$_2$ and 1.7 nm for O KLL.

Oxide thickness was plotted as a function of time and showed a rapid initial rate of oxidation, followed by a slower growth rate approaching a limiting thickness of approximately 2.4 nm (Figure 5). This was in agreement with the observations for O KLL Auger peak intensity behaviour described in Section 3.1. On the basis of the best fit to the experimental data in Figure 5, the oxidation kinetics can be accurately described by a logarithmic rate law (Equation 4), where the oxide thickness, $d$, is given by

$$d = k \log(a + b),$$

(4)

where $k$ is the rate constant and $a$ and $b$ are separate, experimentally determined, constants. The best fit was obtained for the function $d = 1.26 \log(0.12t + 0.56)$.

Previous studies on uranium and uranium alloy oxidation describe parabolic or linear behaviour; however, these tend to be based on gravimetric methods performed at elevated temperatures and atmospheric pressure, which are therefore concerned with much later stages of oxidation.$^{3,47}$ As a result, the oxide thickness is likely to be such that ionic diffusion through the oxide layer is the rate limiting step and parabolic kinetics are expected.$^{48}$ It is generally accepted that at ambient temperatures and for thin films, as demonstrated in this current work, the rate limiting step becomes ionization of oxygen atoms to oxygen ions and hence electron transport across the oxide layer, leading to logarithmic behaviour.$^{48,49}$ The resulting oxide reaches a limiting thickness of 2 to 3 nm, which is often referred to as the "Mott thickness". Although the strict interpretation, according to the Mott-Cabrera theory of oxide growth, is associated with the instantaneous growth of an oxide layer as a result of the intensive field, that exists because of the contact potential difference between...
the metal and the adsorbed oxygen. In the current work, carried out at extremely low \( pO_2 \), it is convenient to recall that the exposure unit (Langmuir) represents the deposition of one monolayer of adsorbate; thus, an exposure of 40 L represents some 40 monolayers of adsorbed oxygen at the metal surface. This provides further support for the formation of oxide anions as the rate controlling step.

## 4 | CONCLUSIONS

- In situ UHV oxidation of a U-5Mo alloy sample studied by AES and XPS has shown good agreement between techniques. Specifically, oxygen signals were first detected at approximately 0.17 to 0.30 L \( O_2 \) (O KLL) and 0.28 to 0.40 L \( O_2 \) (O 1s). Additionally, oxygen peak shifts associated with transformation of chemisorbed oxygen to that within a metal oxide were observed to be in the order of 1.5 eV at between 2.3 and 2.6 L \( O_2 \) for the two techniques.

- Assignments were made for six uranium Auger peaks originating from N and O core electrons. All of these peaks exhibited a shift with oxidation of the uranium metal, which indicates that such shifts could be used for AES chemical state mapping studies in combination with AES/XPS spectroscopic data.

- No peak shift was observed for the Mo 3d peak, indicating that molybdenum does not oxidize during the initial oxidation stages of DU-5Mo. This lack of early oxidation is contrary to observations made for uranium-niobium alloys and indicates a lower level of corrosion protection when uranium is alloyed with molybdenum compared with niobium.

- The U 4f doublet peak exhibited a clear peak shift associated with uranium oxidation. The metallic uranium peaks remained observable throughout the experiment (equivalent to 270 ns at 1 atm), highlighting the approaching to a limiting thickness of the oxide in UHV at 40 L exposure. Stoichiometric \( UO_2 \) was the only uranium oxide formed upon oxidation, as determined primarily by the relative position of the U 4f\(_{5/2}\) main oxide peak and corresponding satellite peak (\( \Delta E_{sp} = 7.0 \)).

- In UHV conditions at ambient temperature, the U-5Mo alloy obeys a logarithmic rate law kinetics, with the best fit to the experimental data for the oxide thickness, \( d \), being given by \( d = 1.26 \log(0.12t + 0.56) \). This oxidation rate behaviour is typical of oxide layer thicknesses in the order of that observed here (approximately 2.4 nm).

## ACKNOWLEDGEMENTS

This work was supported by the EPSRC (grant no. EP/G037388) via the University of Surrey CDT in MINMaT and AWE plc. We thank Professor Jim Castle for helpful discussions.

## DATA AVAILABILITY

All data associated with this paper are held for a minimum of 10 years in accordance with EPSRC regulations and are available upon request.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of the article.

**How to cite this article:** Bacon SR, Brierley M, Baker MA, Watts JF. Oxidation of a depleted uranium-5 wt% molybdenum (U-SmO) alloy in UHV by AES and XPS. *Surf Interface Anal.* 2019;51:849-856. https://doi.org/10.1002/sia.6659