

Plutonium oxide transformation kinetics and diffusion coefficient measurement

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Abstract

When subjected to ultra high vacuum (UHV) conditions, a thin surface dioxide covering on a plutonium metal substrate will undergo a spontaneous, thermodynamically driven, reduction to the trivalent sesqui-oxide, Pu₂O₃. Kinetic information about this surface transformation, from PuO₂ to Pu₂O₃, is gained by following the changing depths of these two oxide layers, using X-ray photoelectron spectroscopy (XPS) as a probe. A mathematical model is proposed to follow this auto-reduction reaction, based on a simple 2D layered structure. The rate of this plutonium oxide inter-conversion is controlled by diffusion of oxygen across the steadily expanding Pu₂O₃ layer. Through investigating the kinetics of this auto-reduction reaction, a value of $1.4 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$ is obtained for the diffusion coefficient of oxygen through α -Pu₂O₃.
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1. Introduction

The highly oxophilic nature of plutonium has the consequence that, under ambient conditions, its surface is completely covered by a tetravalent, PuO₂, oxide layer. In the absence of O₂, PuO₂ is thermodynamically unstable on plutonium metal [1], although even under the stringent conditions of a high quality inert atmosphere dry box (O₂ ~ 1%, H₂O < 1 ppm) the dioxide layer is still found to persist. However, when subjecting plutonium metal samples covered with dioxide to ultra high vacuum (UHV) conditions, the dioxide layer undergoes a spontaneous, thermodynamically driven [1], reduction to the trivalent sesqui-oxide, Pu₂O₃. In this work, kinetic information about the surface transformation, or “auto-reduction” from PuO₂ to Pu₂O₃, is gained by following the changing depths of the two oxide layers, using X-ray photoelectron spectroscopy (XPS) as a probe. Fig. 1 shows a schematic representation of how the plutonium oxides interconvert under both oxygen and UHV environments.

The model proposed for the auto-reduction reaction derives from a simple 2D layered structure, where initially a layer of α -Pu₂O₃ lies between a PuO₂ layer and the Pu metal. When

left under UHV conditions the PuO₂ converts, at its interface with the Pu₂O₃, so that the boundary between the two oxide layers slowly approaches the vacuum interface, and the oxide overlayer is converted to the sesqui-oxide. The observed kinetics are directly related to the diffusion of oxygen through α -Pu₂O₃, and hence, values can be deduced for the diffusion coefficient and activation energy for this process. Effort has been made to confirm that the auto-reduction reaction is neither driven nor influenced by exposure of the sample to the X-rays required to capture the XPS data.

2. XPS analysis

The quantification of plutonium oxide layers with XPS has previously been achieved by Gouder and Havela [2], and within this work a similar, reproducible methodology for fitting the photoionisation peaks of plutonium 4f electronic states has been employed. The binding energies of the plutonium 4f peaks for both oxides are in good agreement with earlier work [3], with 4f_{7/2} peak positions of 426.2 eV and 424.6 eV being observed for PuO₂ and Pu₂O₃, respectively. The PuO₂ peaks are composed of a symmetric Gaussian/Lorentzian doublet, with similar symmetric peaks being used to fit the “shake-up” satellites observed with XPS from the dioxide. The Pu₂O₃ peak shapes are composed from an asymmetric Gaussian/Lorentzian doublet, which

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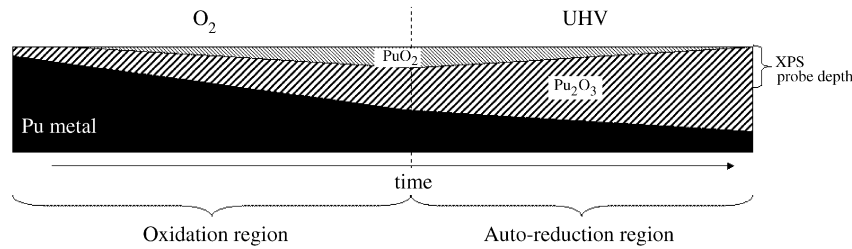


Fig. 1. Demonstrating how the oxides of plutonium grow and interconvert at the surface of a metal coupon, within both oxygen and UHV environments. The figure is based on low-pressure oxygen exposure at ambient temperatures, which results in a relatively thin PuO_2 layer over a thicker underlying Pu_2O_3 layer.

is assumed to consist of unresolved shake-up satellites lying close to the main $4f$ peaks. The contribution from plutonium metal to the $4f$ envelope occurs with a $4f_{7/2}$ peak position at 422.1 eV. The fitting process is carried out using CasaXPS software [4], and incorporates a Shirley [5] background subtraction method. During fitting, only the relative areas attributed to the metal, the sesqui-oxide and the dioxide are allowed to vary, with all the peak positions and FWHM values being constrained. Fig. 2a shows an example of a set of auto-reduction XPS spectra and Fig. 2b shows the corresponding PuO_2 thickness versus time plot.

The layer thickness is calculated using the popular method of Hill et al. [6], with values for the inelastic mean free path (IMFP) calculated using the TPP2 equation [7]. The Hill method of calculating layer thickness relies on the layers being perfectly flat 2D structures. In an attempt to assess whether it is reasonable to assume that the reaction follows a flat 2D geometry, data were collected at different emission angles during the same auto-reduction reaction (following a $\theta = 0^\circ, 30^\circ$ and 50° repeating pattern). An assessment of the gradient of $\text{Ln}(1 + I_r)$ versus $\text{Sec}(\theta)$ for the multiple angle data, where I_r represents the peak area ratio (adjusted for relative emitter atom concentration and

density) and θ is the emission angle, shows that for each data set the gradient is within 5% of that expected for a perfectly flat 2D structure. Furthermore, the multiple angle data, when compared to calculated spectral intensities, confirm without doubt that the PuO_2 layer occurs at the oxide vacuum interface, while the Pu_2O_3 layer exists between the PuO_2 and the metal substrate.

3. Mathematical model

A mathematical model for the auto-reduction of the PuO_2 to $\alpha\text{-Pu}_2\text{O}_3$ is proposed which quantifies the rate of the auto-reduction reaction, the details of which are shown below. This model allows the determination of a parabolic rate constant from the XPS results, and permits comparison between the parabolic rate constants, diffusion coefficients and the activation energy for diffusion, for different plutonium oxides.

By solving for the rate of thickening of the $\alpha\text{-Pu}_2\text{O}_3$ layer during auto-reduction it can be shown that

$$d_{3+} = (kt)^{1/2}, \quad (1)$$

where d_{3+} is the thickness of the $\alpha\text{-Pu}_2\text{O}_3$, t the time, and k the parabolic rate constant for the growth of the $\alpha\text{-Pu}_2\text{O}_3$ layer.

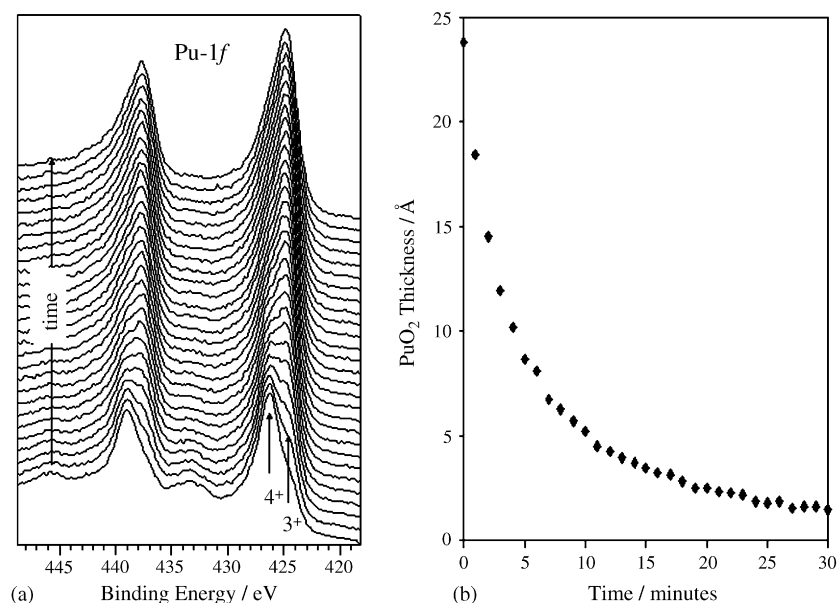


Fig. 2. (a) An example of XPS spectra collected from a plutonium oxide layer while auto-reducing from PuO_2 to Pu_2O_3 , after oxidation at 10^{-7} mbar (some spectra have been excluded for clarity). Note that both 3+ and 4+ components are observed in the initial spectra, indicating that the outer PuO_2 layer is still very thin (approximately 25 Å). (b) The resulting PuO_2 layer thickness versus time plot, obtained through fitting the individual XPS spectra.

However, this assumes that the initial thickness of the α -Pu₂O₃ layer is zero ($d_{3+}^i = 0$), but by applying the general solution for a quadratic equation one obtains the general description for α -Pu₂O₃ layer thickening,

$$d_{3+} = \frac{d_{3+}^i + ((d_{3+}^i)^2 + 4kt)^{1/2}}{2}. \quad (2)$$

Furthermore, at any moment during the auto-reduction reaction, d_{4+} , the PuO₂ layer thickness, is given by,

$$d_{4+} = d_{4+}^i - \frac{d_{3+} - d_{3+}^i}{\lambda}, \quad (3)$$

where λ is a conversion factor to account for the different volumes of the two oxide layers ($\lambda = 1.46$). By substituting Eq. (2) into Eq. (3) one obtains,

$$d_{4+} = d_{4+}^i + \frac{d_{3+}^i - ((d_{3+}^i)^2 + 4kt)^{1/2}}{2\lambda}. \quad (4)$$

We now find that we can model the changes in PuO₂ thickness as a function of constants for the initial oxide thicknesses (d_{4+}^i and d_{3+}^i) and k . It should be noted that t_0 , the time at which oxidation ceases and the auto-reduction reaction dominates, is defined as the time after evacuating the O₂ when the pressure falls below 10⁻⁷ mbar. Deviation is observed between the model and the data as the PuO₂ layer thins, because at reduced thickness the dioxide layer starts to break up into small islands, and the model does not account for this effect. Nor does the model account for the re-oxidation of the thin PuO₂, which, however small, certainly occurs from the background oxidising gases present in the UHV system. Nonetheless, once we have obtained the parabolic rate constant we can derive the diffusion coefficient, which in our case is for oxygen diffusion through α -Pu₂O₃, and previously unmeasured. By making simple assumptions, based on Weber's theory of oxidation [8], we obtain $k = 2D$, where D is the diffusion coefficient. It is also

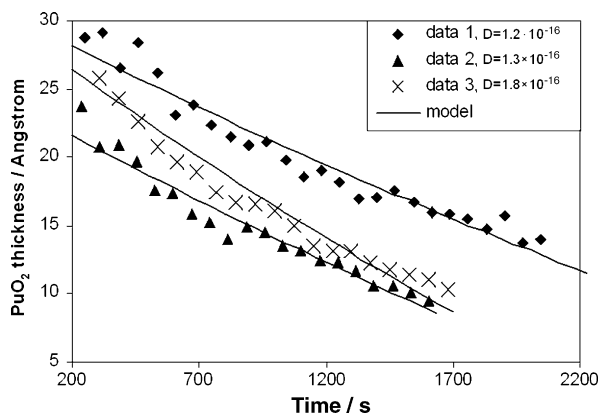


Fig. 3. Results from three repeated auto-reduction reactions followed by measuring the PuO₂ layer thickness by XPS (points) and fitting to a model using Eq. (4) (lines). Prior to evacuating the sample to UHV, to follow the auto-reduction reaction, O₂ exposures were undertaken at 30 °C and $\approx 7 \times 10^{-2}$ mbar for 90 min generating a total oxide thickness of ≈ 200 Å (as in [10]). Good agreement is initially observed between the data and the model, however, the two diverge as the dioxide film thins, breaks into islands, and surface re-oxidation becomes significant.

Table 1

Showing the experimental parameters, the calculated diffusion coefficient, D , and activation energy for diffusion, E_a , for oxygen diffusing through α -Pu₂O₃ (D and E_a were calculated by following the auto-reduction reaction occurring in UHV after oxidation with a dose equivalent to that employed by Larson and Cash [10] to obtain an initial oxide thickness (Pu₂O₃ + PuO₂) of ≈ 200 Å)

| P_{dose} (mbar) | T (°C) | Time (min) | D (cm ² s ⁻¹) | E_a (kJ mol ⁻¹) |
|--------------------------|----------|------------|--|-------------------------------|
| 6×10^{-2} | 30 | 90 | 1.3×10^{-16} | 75.1 |
| 7×10^{-2} | 30 | 90 | 1.2×10^{-16} | 75.4 |
| 7×10^{-2} | 30 | 90 | 1.8×10^{-16} | 74.2 |

possible to deduce the activation energy associated with oxygen diffusion through α -Pu₂O₃, despite data being obtained at a single temperature (30 °C) using a method demonstrated by Stakebake [9] for PuO₂. Comparisons can then be made between oxygen diffusion within these two plutonium oxides.

To measure the diffusion coefficient by the method described above, a significant problem is faced in measuring the initial thickness of the α -Pu₂O₃, since this layer is too thick for XPS to measure. Therefore, we require an alternative method of determining the initial thickness parameters for the PuO₂ and α -Pu₂O₃ layers. This is achieved through comparison to existing data in the literature, specifically the ellipsometry data of Larson and Cash [10]. By choosing identical oxidation parameters to Larson and Cash [10], i.e., O₂ pressure, temperature, and time, we can make the assumption that $d_{4+}^i + d_{3+}^i = 200$ Å; the total oxide thickness measured in the ellipsometry experiments after a 90 min oxidation. Then we simply fit the individual parameters, whilst maintaining the condition $d_{4+}^i + d_{3+}^i = 200$ Å, to the data, and thus, extract the parabolic rate constant, the diffusion coefficient and activation barrier for diffusion of oxygen in α -Pu₂O₃. Fig. 3 shows Eq. (4) being applied to model real experimental data, while Table 1 shows the values obtained after three successive equivalent experiments.

The data in Table 1 gives an average diffusion coefficient, D , of 1.4×10^{-16} cm² s⁻¹ for oxygen diffusing through α -Pu₂O₃, with an average activation energy, E_a , of 74.9 kJ mol⁻¹. The numbers obtained for PuO₂ by Stakebake [9] for oxygen diffusion through PuO₂, at an equivalent temperature to the work here, were $D = 6 \times 10^{-19}$ cm² s⁻¹ and $E_a = 94.6$ kJ mol⁻¹. As expected, oxygen diffusion through PuO₂ is slower than through α -Pu₂O₃, since this form of the sesqui-oxide adopts an equivalent structure to the dioxide but with additional oxygen vacancies. The observed increase in the diffusion coefficient for oxygen diffusing through α -Pu₂O₃, as compared to PuO₂, is around two orders of magnitude, with a corresponding decrease in the activation energy for diffusion by a factor of around 0.8.

4. Conclusions

It has been shown that there is a spontaneous auto-reduction reaction between the dioxide and sesqui-oxide phases of plutonium under UHV conditions. For relatively thin oxide layers, the time for the conversion reaction is of the order of minutes at ambient temperature, and these reaction kinetics have been studied using XPS. A mathematical model based on dif-

fusion kinetics has been applied to the auto-reduction data, and has enabled the determination of both the diffusion coefficient, $1.4 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$, and the activation energy, 74.9 kJ mol^{-1} , for oxygen diffusion through $\alpha\text{-Pu}_2\text{O}_3$.

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