
ARTICLE

Direct mass analysis of water absorption onto thoria thin filmsDominic Laventine^a, Colin Boxall^{a*}, Robin Orr^b and Robin J. Taylor^b^aUniversity of Lancaster, Department of Engineering, Lancaster, LA1 4YR, UK; ^bNational Nuclear Laboratory, Central laboratory, B170, Sellafield, CA20 1PG, UK

Plutonium oxide (PuO₂) is one of the most highly radioactive products of the nuclear fuel cycle and its storage poses particular challenges due to the high temperatures produced by its decay and the production of gases from, *inter alia*, surface adsorbed water entrained with the PuO₂ during the packaging process. Its high radiotoxicity necessitates the use of actinide oxides in similar oxidation states, such as ThO₂, as model systems to allow the comprehensive study of its interaction with water under storage conditions. We have developed a method which enables direct gravimetric measurement of the adsorption of microgram amounts of water onto ThO₂ thin films, also with masses in the microgram range. Porous ThO₂ films were deposited from a surfactant based precursor solution onto thin GaPO₄ crystal substrates. The absorption of water onto the ThO₂ coating at different relative humidities was then studied in a closed reactor using crystal nano-balance gravimetry, wherein changes in crystal resonant frequency due to absorbed mass are directly and linearly related to mass changes occurring at the crystal surface. Using this method, we have determined the enthalpy of absorption of water onto ThO₂ to be 54.6 kJmol⁻¹ at 75°C, 13 kJmol⁻¹ greater than the enthalpy of evaporation. This enthalpy is within the range predicted for the reversible absorption of water onto PuO₂, indicating this method allows for the investigation of water absorption onto plutonia using microgram samples.

Keywords: thoria; plutonium oxide; water absorption

1. Introduction

Plutonium oxide (PuO₂) is one of the most highly radioactive components of nuclear fuel product streams. This poses particular challenges in storing large amounts for reuse as mixed oxide fuel for the next generation of fast reactors, or for eventual deposition into long-term geological storage, which has been proposed at a number of sites worldwide. Interim storage is typically within a series of nested steel canisters under a partially inert atmosphere. These canisters develop high internal temperatures due to the PuO₂ decay heat and have been observed to become pressurised due to the evolution of hydrogen gas and steam from, *inter alia*, surface adsorbed water entrained with the PuO₂ during the packaging process. A greater understanding of PuO₂ interaction with water is therefore imperative to allow the design of safe long-term storage facilities [1-4].

Thoria (ThO₂) is widely employed as a model substrate for radioactive metal oxides such as plutonium oxide, due to the metals' similar ionic radii and stable oxidation states and the oxides similar fluorite structure. Thoria polycrystals exhibit a significant absorption of water vapour at temperatures up to 600°C [5], and previous studies have indicated this to be true of

plutonium oxide. The absorption of water results in numerous physio- and chemi-adsorbed layers, but the subsequent fate of this water under elevated temperatures and pressures and in the presence of highly radioactive material is unknown. Water adsorption on PuO₂ has been previously investigated by measuring headspace pressure, as a function of temperature within a closed system containing a fixed quantity of PuO₂ in the presence of varying amounts of deliberately added water [6-8]. This involves making a number of assumptions relating to the PVT behaviour of the headspace of the closed system, usually based on the behaviour of an ideal gas, in order to estimate the mass of water adsorbed at the PuO₂ surface [8,9].

We have developed a method that enables direct gravimetric measurement of water adsorption onto ThO₂ thin films. We have previously reported the use of Quartz Crystal Microbalance (QCM) gravimetry as a signal transducer, as changes in crystal resonant frequency are directly related to mass changes occurring at the crystal surface at ambient temperatures [12]. In this work, *ortho*-gallium phosphate (*o*-GaPO₄) crystals were used instead of quartz due to the linear temperature-dependence of their resonant frequency as well as their higher piezoelectric limiting temperature [7], allowing the absorption of water to be analysed

*Corresponding author. Email: C.Boxall@lancaster.ac.uk

under the temperature conditions that develop in typical PuO_2 storage conditions of up to 600°C . Herein, we describe preliminary experiments in the coating of $o\text{-GaPO}_4$ crystal electrodes with nano-scale crystalline ThO_2 films and measurements of their absorption of water.

2. Experimental

2.1. Materials and reagents

All reagents used are AnalaR grade or higher, and purchased from Sigma Aldrich (Gillingham, Dorset, UK). All water used is Ultrapure doubly de-ionised water from a Direct-Q 3 UV Millipore water purification system (Millipore (U.K.) Limited, Watford, UK) to a resistivity of $18.2 \text{ M } \Omega\cdot\text{cm}$. Nitrogen Whitespot grade (moisture content 3 ppm) is provided by BOC Ltd., Guildford, Surrey, UK. All $o\text{-GaPO}_4$ crystals used had a resonant frequency of 6 MHz and were coated on each side with platinum electrodes. The electrodes had a piezoelectrically active area of 0.64 cm^2 . The crystals were purchased from Piezocyst GmbH, Austria. The heater, vessel and controller were purchased from Scientific and Medical Products, Cheadle, UK and had a system accuracy of $\pm 1^\circ\text{C}$.

2.2. Methods

A ThO_2 film was deposited on $o\text{-GaPO}_4$ crystals using an adapted version of the Lundberg method for generating thin films of crystalline ThO_2 [10]. A stock solution of 8.4 mM of $\text{Th}(\text{NO}_3)_4$ in 5% nitric acid (aq.) was created. 25 μl of this solution mixed with 25 μl of oxalic acid in water (25.2 mM) and agitated for 5 minutes. The resulting dispersion were drop-coated onto one electrode surface of $o\text{-GaPO}_4$ crystals and allowed to evaporate in air, then calcined in air at 650°C for 5 h, resulting in formation of white layers adhered to the platinum piezoelectrode surface.

The formation of crystalline ThO_2 was confirmed by Raman spectroscopy and by XRD analysis of the layers. The morphology of the layers was investigated using a PhenomTM scanning electron microscope (Lambda Photometrics, Herfordshire). ThO_2 -coated crystal electrodes were mounted into commercially available crystal holders (Colnatec, US) constructed of steel and ceramic leaving only the coated crystal face accessible. The crystal mount was suspended within a steel reaction vessel (vol = 1 L) such that it was not in contact with any internal surface. A stream of dry nitrogen was passed into an inlet port on the reaction vessel and allowed to escape from an exhaust port while the vessel was heated in a furnace to $\sim 400^\circ\text{C}$. This procedure continued for 6+ hours, or until the observed frequency of the crystal remained steady. The system was then sealed and allowed to return to RT and the baseline frequency recorded. A defined amount of water was added by microsyringe and the system was then re-sealed and the frequency and temperature recorded

every second. As the water added to the system evaporated and redeposited onto the crystal surface, the frequency (inversely proportional to mass) was observed to drop. Once a steady frequency was reached, the system was temperature cycled from RT to $\sim 350^\circ\text{C}$ with continuous recording of the temperature and corresponding frequency. Once at RT again, the gas inlet was re-attached and a slow stream of nitrogen passed through the system until the frequency stabilises. The above procedure was then repeated (from the initial heat cycling) with a different amount of water added.

3. Results and discussion

The layers formed by drop-coating and calcination were found to be strongly adhered to the platinum electrode surfaces of the $o\text{-GaPO}_4$ crystals, being resistant to manual abrasion. SEM imaging showed the layer to be comprised of a rough surface of ThO_2 with numerous voids and pores present (Figure 1).

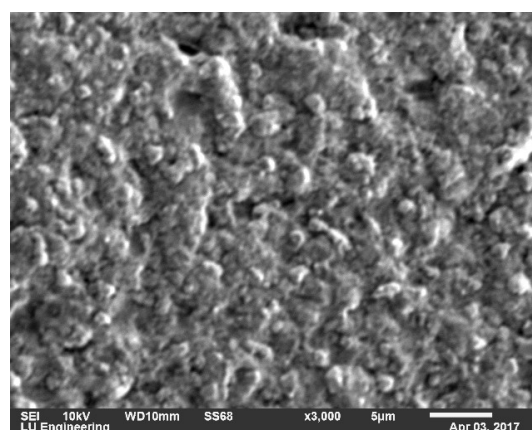


Figure 1. SEM image of a ThO_2 film on a platinum / $o\text{-GaPO}_4$ piezoelectrode.

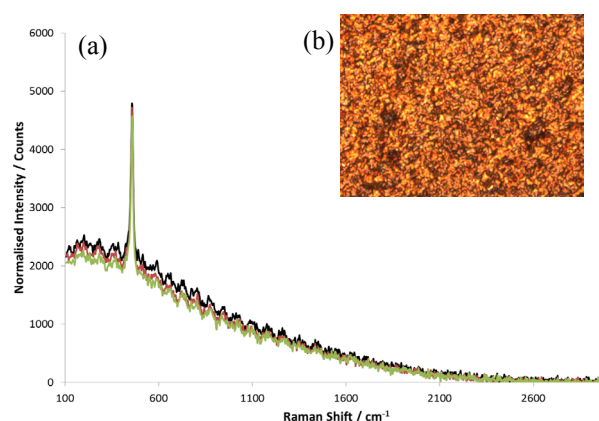


Figure 2. (a) Raman spectra of ThO_2 layer measured at 3 points, showing characteristic fluorite-structure peak at 460 cm^{-1} [11], (b) inset of microscope image at 50x magnification.

Raman spectroscopy (785 nm excitation) showed a characteristic ThO_2 fluorite-structure peak at 460 nm (Figure 2) [11]. XRD analysis of a powder sample

produced under the same conditions evinces characteristic peaks for crystalline ThO₂ (Figure 3) [12].

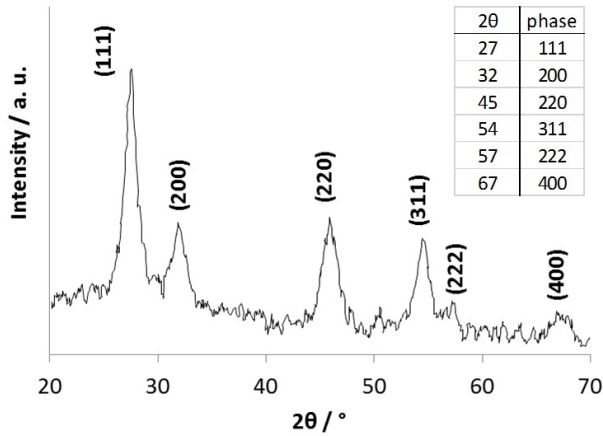


Figure 3. XRD plot of ThO₂ powder produced by evaporation of Th(oxal)₂ dispersion and calcination at 650 °C for 5 h, showing characteristic ThO₂ peaks [12].

Deposition of the ThO₂ layers resulted in a resonant frequency drop of 5214 Hz, equating to a 68 μg increase in mass using a conversion factor of 7.68 × 10⁷ Hz.cm².g⁻¹ calculated using the Sauerbrey equation (eqn. 1) [13]. This is below the 2% threshold at which the Sauerbrey equation becomes unreliable to describe mass changes occurring at the composite resonator surface.

$$\Delta f = - \left(\frac{2 n f_0^2}{A \sqrt{\rho_q \mu_q}} \right) \Delta m \quad (1)$$

Using the area of the crystal electrode coated and the density of bulk thoria (9.70 g.cm⁻³) [14], the layers were estimated to be 116 nm thick, assuming a homogenous non-porous coating with ideal geometry.

Initial microbalance experiments with the coated crystals were conducted at 75°C. It was found that the resonant frequency of the coated crystals reduced in response to the addition of water to the system, corresponding to a 4.6 μg mass increase per coated crystal (approximately 135 mg of water absorbed per gram ThO₂ layer) at 100% relative humidity. The relative humidity was varied by changing the amount of water added to the system and maintaining the temperature at a constant 75°C. It was found the amount of water absorbed onto the thoria coating increased with increasing partial pressure of water. A plot of this change in frequency or mass against the partial pressure resulted in a graph typical of a type II adsorption isotherm (Figure 4). Addition of further water to the already saturated system resulted in a linear increase in the mass of water detected on the crystal due to simple physical deposition. The BET equation (Eq. 2) can be used to calculate the enthalpy of adsorption (ΔH_{ads}) and the volume of a monolayer of molecular water adsorbed onto a surface:

$$1/\left[V_a \left(\frac{P_0}{P} - 1\right)\right] = \left(\frac{C-1}{V_m C}\right) \left(\frac{P}{P_0}\right) + \frac{1}{V_m C} \quad (2)$$

where V_a is the volume of adsorbed water, P and P_0 are the equilibrium and saturation pressure of water at the temperature of adsorption, V_m is the volume of an adsorbed monolayer and $C = \exp(\Delta H_{\text{ads}} - \Delta H_{\text{liq}}/RT)$. A plot of $p/V_a(P_0 - P)$ versus P/P_0 yields a straight line, the slope of which is $(C - 1)/(V_m C)$ and intercept is $1/V_m C$. The BET equation is typically only valid up to pressures of approximately $P/P_0 = 0.35$; the BET plot for H₂O adsorption in this range produces a straight line, with R² values of 0.997 (Figure 5). Least-square regression analysis of this line gives a slope of 5.26 × 10¹¹ with a standard error of 0.21 × 10¹¹.

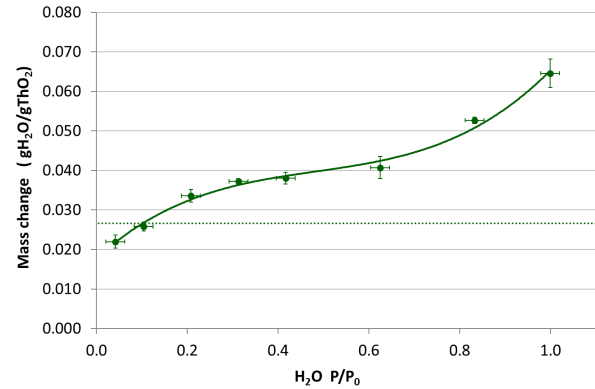


Figure 4. Change in mass of water absorbed per gram of ThO₂ with increasing partial pressure of water. The dotted line shows the calculated mass of a monolayer of water per gram of ThO₂. Horizontal error bars represent the limit of precision of measurement; vertical bars represent the standard deviation from the mean.

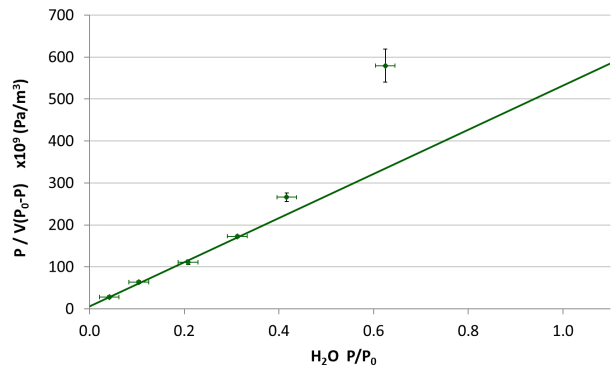


Figure 5. BET plot of water absorption onto ThO₂-coated crystals, with gradient 5.26 × 10¹¹ Pa.m⁻³ and intercept 6.37 × 10⁹ Pa.m⁻³. Trendline and values are calculated from the measurements up to $P/P_0 = 0.35$ [15].

The volume of an adsorbed monolayer of water on the ThO₂ films was calculated to be 1.88 ± 0.08 × 10⁻¹² m³ (2.66 ± 0.11 × 10⁻⁸ m³.g⁻¹ ThO₂). Using a literature estimate for the footprint of a molecule of water of 1.60 × 10⁻¹⁹ m² [10], this corresponds to an accessible surface area of 1.00 ± 0.04 × 10⁻² m² (142 ± 6 m².g⁻¹ ThO₂). The ΔH_{ads} for water adsorption can also be calculated: Taking the ΔH_{liq} of water at 75°C to be 41.8 kJmol⁻¹, ΔH_{ads} for H₂O on ThO₂ was calculated to be 54.6 ± 1.3 kJmol⁻¹. This value is above the range proposed by Paffett *et al.* for reversible H₂O adsorption on PuO₂ of

between 44 and 51 kJmol⁻¹ [8], which suggests that molecular water adsorbed on ThO₂ prepared by this method is bound more strongly than on PuO₂.

4. Conclusion

We have developed a QCM based method for measuring water adsorption on ThO₂, in closed conditions. In our system, an *o*-GaPO₄ piezocrystal is coated on one face with a voided ThO₂ film. Water adsorption on ThO₂ was measured by introducing various amounts of water into the vessel at 75°C, resulting in a range of humidities up to the saturation vapour pressure. It was found that up to 4.6 µg of H₂O adsorbs on the ThO₂ film at 75°C and 100% relative humidity. We have determined the enthalpy of absorption of water onto ThO₂ to be 54.6 kJmol⁻¹ at 75°C, 13 kJmol⁻¹ greater than the enthalpy of evaporation. This enthalpy is higher than the range predicted for the reversible absorption of water onto PuO₂, [9, 16], indicating the water is bound more strongly. Work continues to study the absorption of water onto ThO₂ at higher temperatures to discover the point at which all water is desorbed. Plans are also currently underway to apply this method directly to PuO₂ samples.

Acknowledgements

The authors would like to acknowledge the EPSRC (Award No. EP/L014041/1), The National Nuclear Laboratory and Nuclear Decommissioning Authority (Agreement No. 1006049) and the Lloyd's Register Foundation (LRF) for funding. LRF supports the advancement of engineering-related education, and funds research and development that enhances safety of life at sea, on land and in the air.

References

- [1] International Atomic Energy Agency, IAEA Annual Report for 1998, (1999), pp. 99-1041.
- [2] J.L. Stakebake, J. McClard and R.W. Szempruch, Stabilization and packaging of plutonium oxide for 50-year storage, *Abstracts of Papers of the American Chemical Society*, 219 (2000), pp. U70-U70.
- [3] N.C. Hyatt, Plutonium management policy in the United Kingdom: The need for a dual track strategy, *Energy Policy*, 101, (2017), p.303.
- [4] U.S.D.o. Energy, Assessment of plutonium storage safety issues at department of energy facilities, DOE/DP-0123T (1994).
- [5] X. Montagne, J. Lynch, E. Freund, J. Lamotte and J.-C. Lavalley, A study of the adsorption sites on thoria by scanning transmission electron microscopy and fourier-transform infrared spectroscopy. Adsorption and desorption of water and methanol, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 83 (1987), p.1417.
- [6] J.L. Stakebake, Thermal desorption study of surface interactions between water and plutonium dioxide, *Journal of Physical Chemistry*, 77 (1973), p.581.
- [7] J.L. Stakebake and L.M. Steward, Water vapor adsorption on plutonium dioxide, *Journal of Colloid and Interface Science*, 42 (1973), p.328.
- [8] M.T. Paffett, D. Kelly, S.A. Joyce, J. Morris and K. Veirs, A critical examination of the thermodynamics of water adsorption on actinide oxide surfaces, *Journal of Nuclear Materials*, 322 (2003), p.45.
- [9] J.M. Haschke, T.H. Allen and J.L. Stakebake, Reaction kinetics of plutonium with oxygen, water and humid air: Moisture enhancement of the corrosion rate, *Journal of Alloys and Compounds*, 243 (1996), p.23.
- [10] P. Murphy, C. Boxall, R. Taylor and D. Woodhead, Investigation of water adsorption on metal oxide surfaces under conditions representative of PuO₂ storage containers, *ECS Trans.* 53 (2013), p.81.
- [11] A. Jayaraman, G.A. Kourouklis and L.G. Vanuiter, a high-pressure raman-study of ThO₂ to 40 Gpa and pressure-induced phase-transition from fluorite structure, *Pramana*, 30 (1988), p.225.
- [12] R. Zhao, L. Wang, Z.F. Chai and W.Q. Shi, Synthesis of ThO₂ nanostructures through a hydrothermal approach, *Rsc Advances*, 4 (2014), p.52209.
- [13] S. Jakab, S. Picart, B. Tribollet, P. Rousseau, H. Perrot and C. Gabrielli, Study of the dissolution of thin films of cerium oxide by using a gapo4 crystal microbalance, *Analytical Chemistry*, 81 (2009), p.5139.
- [14] P. Patnaik, *Handbook of Inorganic Chemicals*, McGraw-Hill, (2003).
- [15] D. Dollimore, P. Spooner and A. Turner, The bet method of analysis of gas adsorption data and its relevance to the calculation of surface areas, *Surface Technology*, 4 (1976), p.121.
- [16] S. Hayun, T.Y. Shvareva and A. Navrotsky, Nanocerium - energetics of surfaces, interfaces and water adsorption, *J. Am. Ceram. Soc.* 94 (2011), p. 3992.