

Dissolution of ceria thin films

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ABSTRACT

Ceria thin films were deposited *via* pulsed laser deposition on to inert alumina (Al_2O_3) substrates with a grain size of 28.6nm. The films were found to be strongly textured in the (111) direction. *Ex-situ* dissolution studies of the films were carried out for a range of aqueous environments using synchrotron-based X Ray absorption spectroscopy. The absolute thickness loss on the film was assessed using the intensity of the fluorescent signal in the XANES region with a significant intensity drop found for the post-treatment films as compared to the pre-treatment ones. The dissolution rate was found to be similar for acids of the same pH but different anion (*i.e.* HCl and H_2SO_4) suggesting that no complexation took place. In an attempt to mimic an oxidizing environment additions of H_2O_2 were added to the acid. The XANES spectra of the pre- and post-treatment films were compared and no changes were observed, indicating that there is no change in the chemistry of the residual material despite the surface reduction required for CeO_2 dissolution.

INTRODUCTION

It is important to understand the behaviour of spent nuclear fuel over long timescales which necessitates quantitative and mechanistic understanding of the fuel in aqueous environments. Some work has been carried out on the fundamental behaviour of PuO_2 in aqueous environments (1) and also on mixed oxide (MOX) fuels (2), which contains significant amounts of PuO_2 . Similar studies of ceria, a potential surrogate for PuO_2 , are lacking. This paper reports an attempt to quantitatively measure the dissolution rate of CeO_2 .

One method that can be used to assess the dissolution mechanism and kinetics of a material is X-Ray Absorption Spectroscopy (XANES and EXAFS). This approach, under appropriate conditions, provides information regarding the valence state and local chemical environment as well as a measure of the rate of dissolution with monolayer levels of sensitivity (3,4).

EXPERIMENTAL

The ceria films were prepared on alumina substrates (SurfaceNet GmbH) (10mm x 10mm) via pulsed laser deposition (PLD), which is described in detail elsewhere (5) and shown schematically in Figure 1.

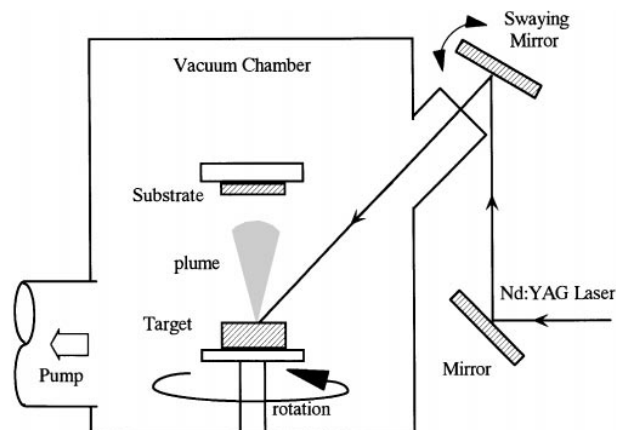


Figure 1 Method of operation for pulsed laser deposition (PLD) (6)

Briefly, PLD consists of using a Nd:YAG laser to vaporize a CeO_2 target in a vacuum producing a plume which then impinges on a substrate in the vapour path. By pulsing the laser it is possible to grow films as multiple layer deposits.

The films were grown using a vacuum chamber in which initially an atmosphere of 3×10^{-5} Torr was established before heating the substrate to 700°C . The surface of the ceria target was then cleaned by pulsing the laser 300 cycles while a shutter within the chamber was used to block the plume from reaching the substrate. The O_2 pressure was then raised to 50 mTorr before the shutter was removed and the laser pulsed for a pre-defined number of times (1500, 3000 or 6000). The

deposited film and substrate were then allowed to cool at a rate of $10^{\circ}\text{C}\cdot\text{min}^{-1}$ until 200°C and then allowed to cool naturally.

The films were characterised using X-Ray Diffraction with a Phillips X'Pert MPD using $\text{Cu K}\alpha$ radiation ($\lambda=1.5409 \text{ \AA}$). To measure the XANES spectra for both pre- and post-treatment films deposited films were immersed into the solution of interest so that half of the film was exposed and half was not. This gave regions which were treated and untreated on the same sample and allowed a direct comparison of their behaviour, eliminating errors associated with any possible differences between samples.

X-Ray spectroscopy experiments using the Ce L_{III} edge (5.723 keV) were performed on BM26 at the ESRF using a fluorescence detector. The beam was focused onto a static point within the hutch so the samples were mounted on a moveable stage which was moved in the x-axis. A bare alumina substrate was used to cover the region which was not of interest and prevent any unwanted fluorescent emission reaching the detector. The schematic is shown in Figure 2

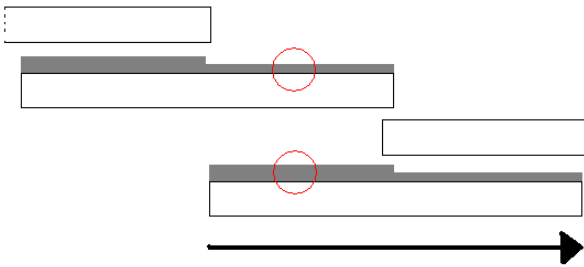


Figure 2 Method used for XAFS and XANES measurements. Grey represents the ceria film, white represents the alumina substrate and the arrow indicated the x-axis. The circles show the location of the X-ray beam and the detector was located above the sample.

RESULTS

Figure 3 shows the XRD scan for the alumina substrate which was confirmed to be α -alumina with preferred orientation of the $\{11\bar{2}0\}$ planes with a less intense $(11\bar{2}6)$ peak also being detected.

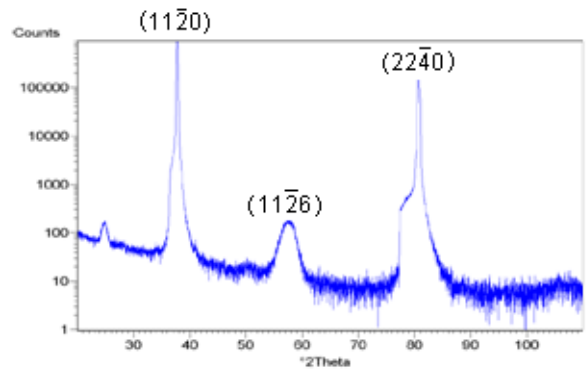


Figure 3 XRD pattern for un-deposited substrate. $(11\bar{2}0)$, $(11\bar{2}6)$ and $(22\bar{4}0)$ orientations were detected.

Figure 4 shows the XRD pattern for the CeO_2 film, where it can be seen that peaks are present which correspond to the $\{111\}$ and (200) CeO_2 planes. No unattributed additional peaks were detected (within the detection limit $<5\%$). From these data it is clear that ceria films have grown on alumina substrates with preferential growth of $\{111\}$ planes with a small amount of (200) growth. Scherrer analysis of the data for the (111) peak gives a grain size of 28.6 nm .

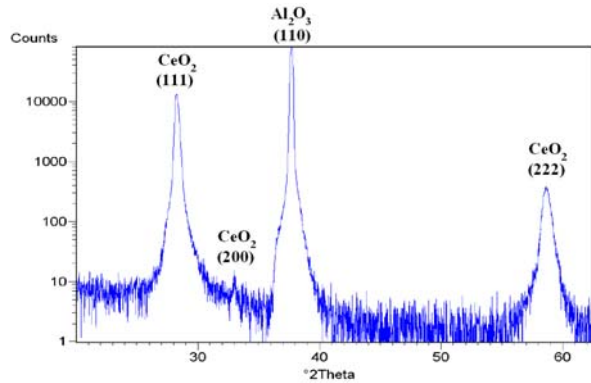


Figure 4 XRD pattern for ceria deposited onto Alumina substrate. In addition to the (110) alumina peak the ceria (111) , (200) and (222) peaks were detected.

The method described previously was then used to assess the dissolution of these films in various media: Figure 5 shows a typical finding from these studies - with the intensity of the signal post-treatment (30 minutes in $10^{-3} \text{ M H}_2\text{SO}_4$) being lower than that of the un-treated sample. This intensity loss can be converted to an equivalent loss of thickness and therefore rate. In this case the value was determined as $3.64 \text{ nm}\cdot\text{minute}^{-1}$.

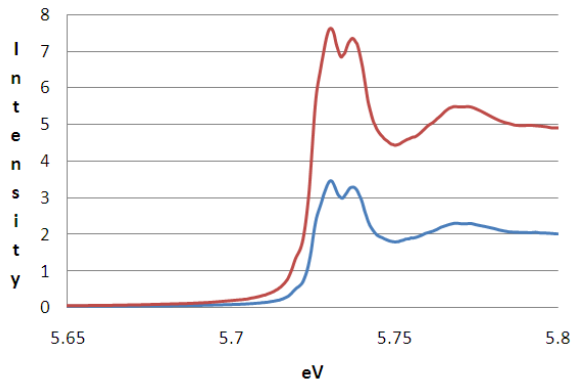


Figure 5 Pre- and post-treatment for 10^{-3} M H_2SO_4 for 30 minutes

The decrease in signal intensity corresponding to a loss in film thickness was observed to increase in a non-linear fashion, by increasing the exposure time to the acidic environment. Figure 6 shows a XANES scan for the same sample as in Figure 5 however re-immersed in the same solution (10^{-3} M H_2SO_4) for a further 10 minutes. There was an increase in the total measured thickness loss (111nm compared with 109nm) however the rate of dissolution for the longer exposure was lower, at $2.78 \text{ nm}\cdot\text{minute}^{-1}$ compared to $3.64 \text{ nm}\cdot\text{minute}^{-1}$. This increase is not significant given the method of calculation, as the film thickness can vary by more than 1nm.

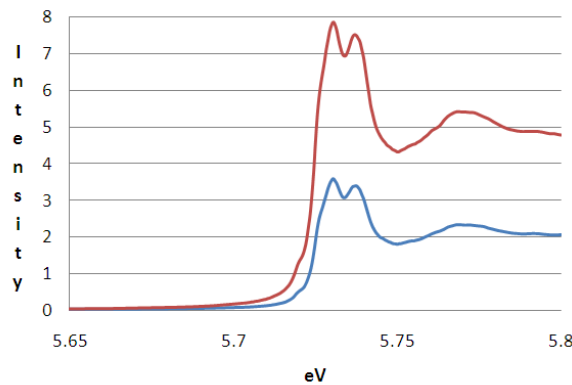


Figure 6 Pre- and post-treatment scans for 10^{-3} M H_2SO_4 for 40 minutes.

Figure 7 shows the pre- and post-treated XANES measurements for a film treated in 10^{-3} M HCl for 30 minutes. The rate of loss was similar ($3.22 \text{ nm}\cdot\text{minute}^{-1}$) to Figure 5 ($3.64 \text{ nm}\cdot\text{minute}^{-1}$), showing the effect that 10^{-3} M H_2SO_4 has over 30 minutes.

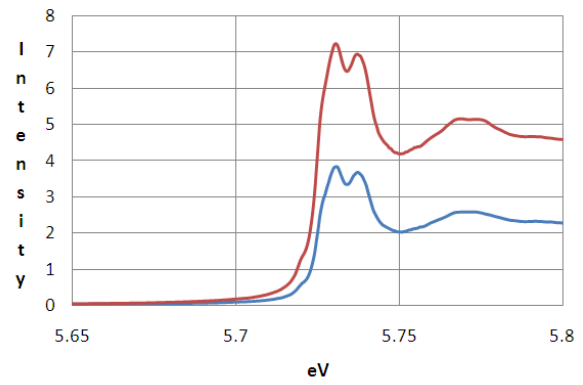


Figure 7 Pre- and post-treatment scans for 10^{-3} M HCl for 30 minutes.

The effect of an oxidizing environment on the dissolution rate was investigated through the addition of H_2O_2 to the acid solution (50% 0.1M H_2O_2 and 50% 10^{-3} M H_2SO_4 (by volume)), Figure 8. The rate of loss was lower for this solution, $1.34 \text{ nm}\cdot\text{minute}^{-1}$, than for 10^{-3} M H_2SO_4 however the decrease in rate could either be due to the decrease in $[H^+]$ or the H_2O_2 inhibiting the dissolution.

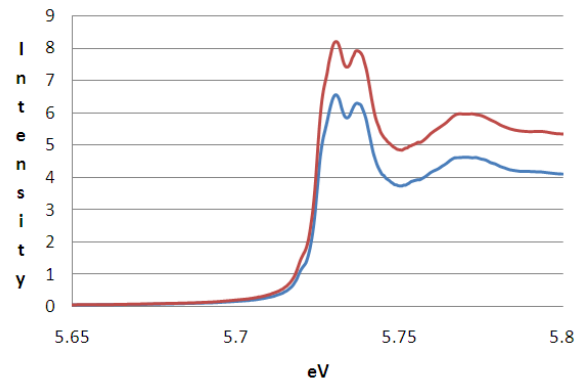


Figure 8 Pre- and post-treatment scans for a 50-50 mixture of 10^{-3} M H_2SO_4 /0.1M H_2O_2 for 30 minutes.

The effect of lower pH was investigated by submersing a film in 10^{-5} M H_2SO_4 for 4 hours. The XANES measurements for this (Figure 9) show a rate of loss, $0.38 \text{ nm}\cdot\text{minute}^{-1}$, which is lower than for dissolution with 10^{-3} M acid of the same type.

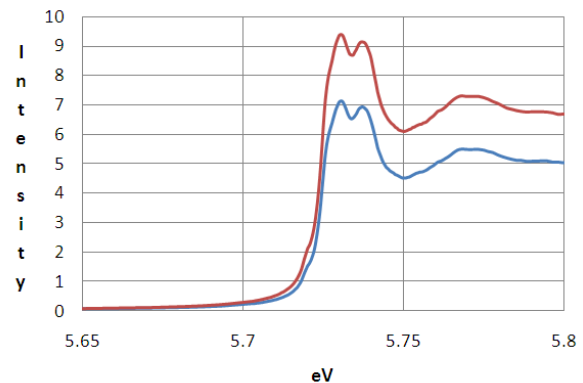


Figure 9 Pre- and post-treatment scans for 10^{-5} M H_2SO_4 for 4 hours.

It was found that there was no change in the XANES features for the pre- and post-treatment films (Figure 10). The peaks indicate that Ce^{4+} is the species present (7), the lack of observed Ce^{3+} could indicate it enters solution and is not retained within the film. This is plausible given the dense nature of the film and the definitive decrease in film thickness.

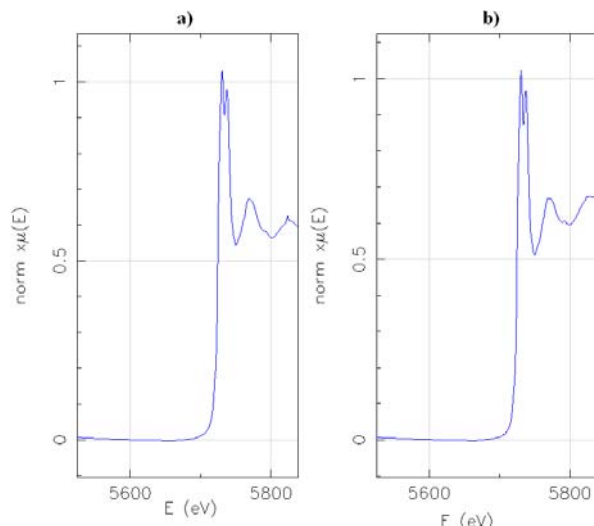


Figure 10 Normalized XANES data with background removed for a) non-treated film and b) film exposed to pH3 H_2SO_4 for 40 minutes. The peak energies for these peaks are 5.723 and 5.737 keV.

A summary of the conditions used, the total intensity loss (determined from the intensity at 5.73 keV) and the calculated dissolution rate is shown in Table 1.

Table 1 - Summary of synchrotron experiments

Conditions	Signal Loss	Figure	Rate (nm.min ⁻¹)
$10^{-3}\text{M H}_2\text{SO}_4$ (30m)	54.6%	Figure 5	3.64
$10^{-3}\text{M H}_2\text{SO}_4$ (40m)	55.5%	Figure 6	2.78
10^{-3}M HCl (30m)	48.3%	Figure 7	3.22
$10^{-3}\text{M H}_2\text{SO}_4/0.1\text{M H}_2\text{O}_2$ (30m)	20.1%	Figure 8	1.34
$10^{-3}\text{M H}_2\text{SO}_4$ (4h)	23.0%	Figure 9	0.38

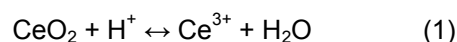
DISCUSSION

Figure 10 reveals no change in either the energy or shape of the XANES band indicating that there is no chemical change in the residual material. For both cases the cerium was in the +4 valence state, consistent with a $\text{CeO}_{2.00}$ structure.

From the evidence gathered in this study it is not possible to say whether the dissolution rate is linear or non-linear. When a comparison was made between the intensity loss for a film held in H_2SO_4 for 30 minutes, then the same film re-immersed for a further 10 minutes, the respective losses showed a small decrease (109nm to 111nm) but not the

additional 1/3 loss that could be expected if the behaviour was linear. Possible reasons for this could be due to the solubility limit of ceria being reached or heterogeneous ease of dissolution meaning that the more soluble material has entered solution leaving only low solubility material, therefore slowing the rate. However, these are only preliminary results and *in-situ* dissolution studies are planned to allow a real-time measurement on static samples. We have been awarded time at the DIAMOND synchrotron and plan to study this effect.

It was also found that similar amounts of loss were observed for different acids of the same molarity as seen in Figure 5 and Figure 7 ($10^{-3}\text{M H}_2\text{SO}_4$ and HCl respectively). This is consistent with the assumption that the mode of dissolution is (8):



There was a slight difference in the rate for HCl ($3.22 \text{ nm}\cdot\text{minute}^{-1}$) and H_2SO_4 ($3.64 \text{ nm}\cdot\text{minute}^{-1}$) (Figure 7 and Figure 5). It is possible that the different ion complexes or cerium salts resulting from the use of different acids change the rate at which dissolution occurs.

The rate for the same acid at different molarities was also investigated: $10^{-5}\text{M H}_2\text{SO}_4$ (Figure 9) and $10^{-3}\text{M H}_2\text{SO}_4$ (Figure 5). For the 10^{-5}M solution the rate was $0.38 \text{ nm}\cdot\text{minute}^{-1}$ whereas the 10^{-3}M solution had rate of $3.64 \text{ nm}\cdot\text{minute}^{-1}$. This rate for the weaker solution was an order of magnitude lower.

CONCLUSIONS

We have shown that it is possible to conduct X-ray spectroscopy experiments of ceria thin films which can potentially be used to better understand the aqueous behaviour of ceria, a material which can be used as a surrogate for PuO_2 .

We have detected dissolution over a range of conditions (10^{-3}M to 10^{-5}M) and for different acid types (HCl and H_2SO_4). This study demonstrates that these thin film dissolution studies are feasible and the methods used can be applied in realtime *in-situ* experiments which will give quantitative dissolution rate information in response to environmental conditions.

FURTHER WORK

We plan to carry out *in situ* dissolution experiments at the DIAMOND facility to investigate the influence of pH, exposure time and acid type on the dissolution rate of CeO_2 thin films. Also, FIB sections from the films used in this study will be produced for TEM analysis.

ACKNOWLEDGEMENTS

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