The Durability of Spent MOX

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INTRODUCTION

MOX fuel is used as a source of energy in fission processes. It is necessary to store and permanently dispose of it after the useful life has ended and for this to be done safely it is important that the processes occurring and behaviour of the fuel in an aqueous environment , as is possible in both storage and disposal, are well understood. A strong mechanistic understanding is required for this.

The purpose of this project is to attempt to achieve this by using CeO_2 as a surrogate for PuO_2 and manufacturing $(U\text{-}Ce)O_2$ simulant MOX. In order to interpret these results the dissolution behaviour of CeO_2 needs to be better understood, to this end dissolution studies on a CeO_2 model system are being carried out on CeO_2 thin films of thickness 200nm.

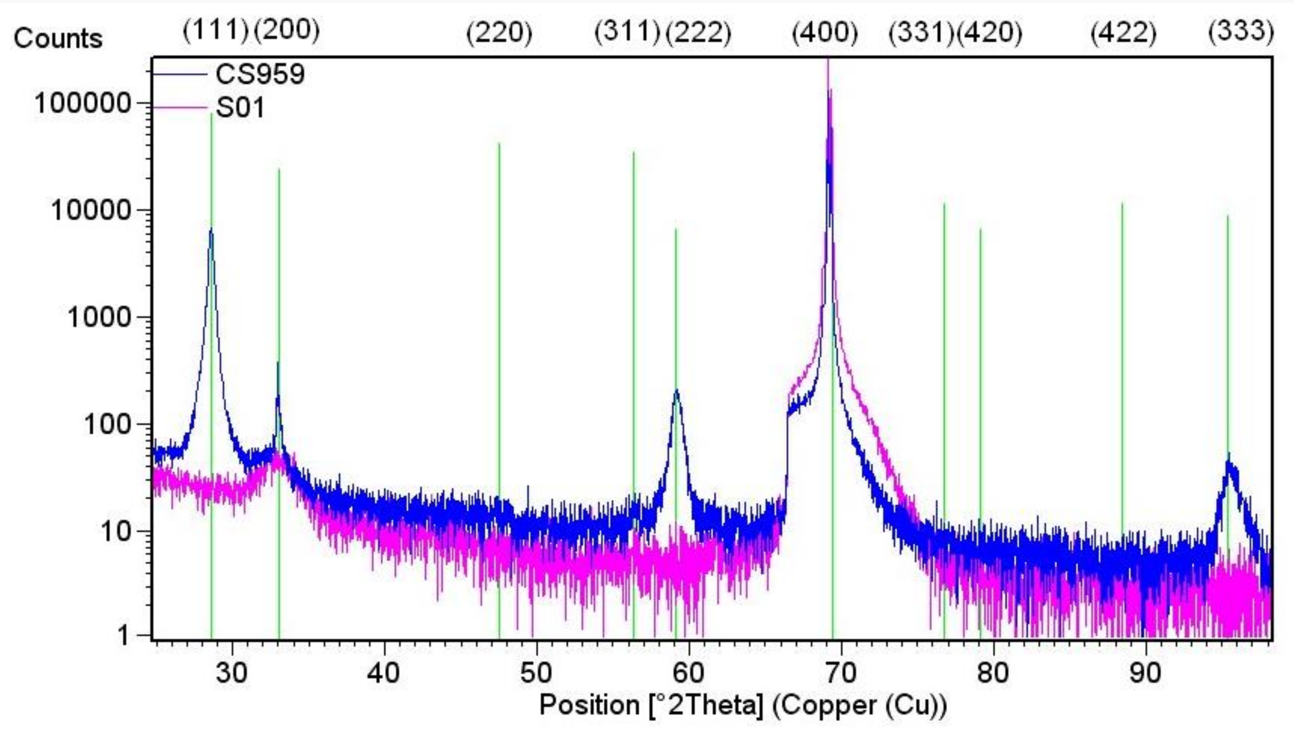

Figure 1 – Θ-2Θ scan of ceria thin film deposited onto a silicon substrate. The blue trace is the film and substrate , the red trace is the substrate itself. The ceria orientations detected are (111), (222) and (333), all of which are parallel to each other. The Si film gives only a (400) reflection.

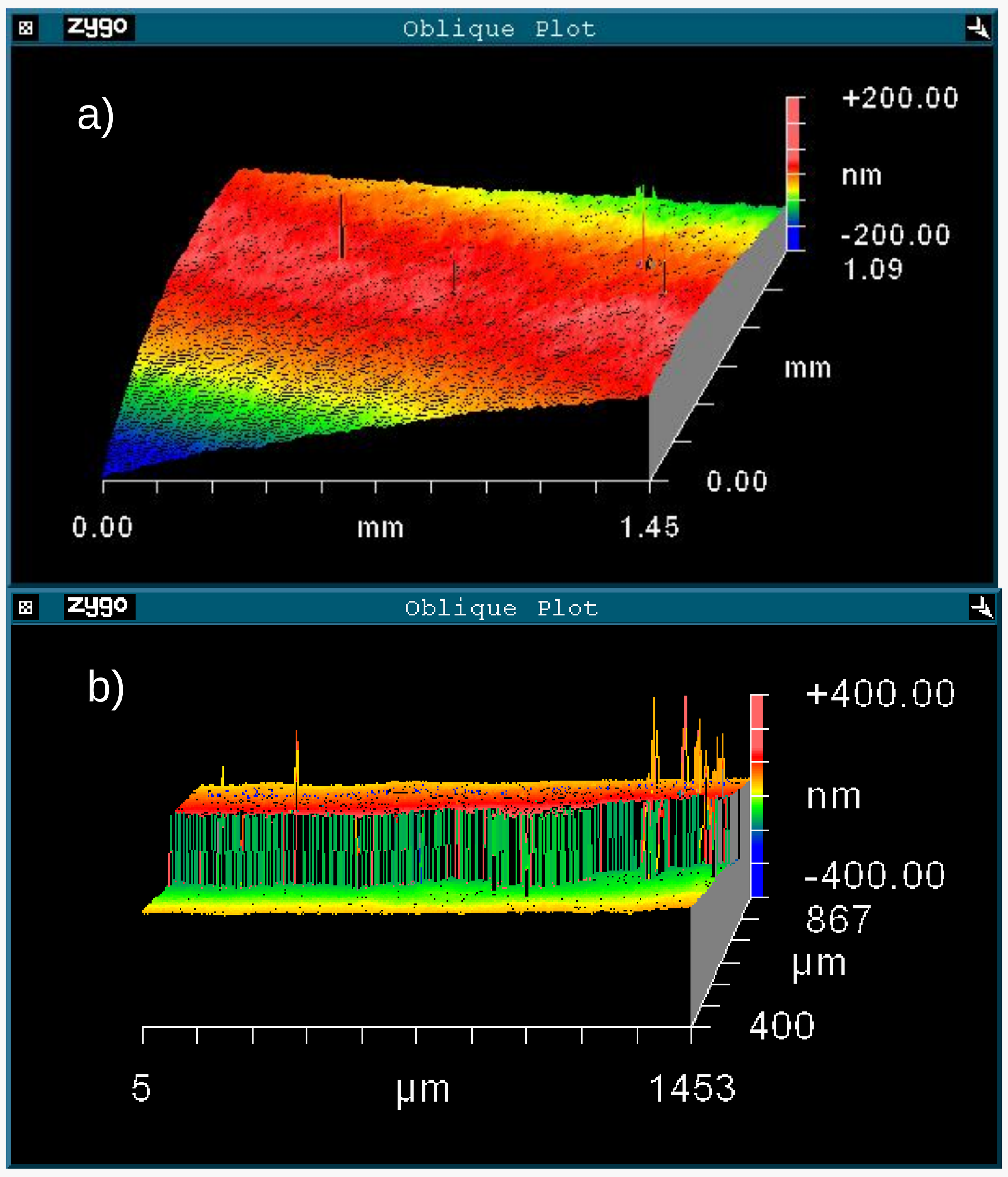

Figure 2 – White Light Interferometry of ceria-silicon films. a) surface of ceria thin film shows a relatively smooth surface, the wave like morphology is taken from the Si substrate.
b) film surface after being immersed in HCl for 24 hours. The size of the step in the image is around 200 nm, the same as the total thickness of the film.

MOX Fuel

Mixed Oxide (MOX) fuel is composed of uranium (90-95%) and plutonium (5-10%). It is manufactured by the Short Binderless Route (SBR) or the Minimization MAximiSation (MIMAS) technique. The attractions of MOX are that spent uranium fuel can be reprocessed to produce it meaning that more energy can be extracted from the same original mass of fuel which would otherwise need to be disposed of.

Once the fuel cycle has ended there is a need to store or dispose of the spent fuel. It is important that the long term performance of the fuel is understood and predictable 1000's of years into the future. To achieve this direct experimental results will not be sufficient, they need to be extrapolated out over geological timeframes. This is only possible by having a sound mechanistic understanding of the processes which are occurring when MOX is exposed to an aqueous environment.

Given the difficulties of working on genuine MOX the approach which has been set on is to use simulant MOX of $(U\text{-}Ce)O_2$.

Ceria as a Puo_2 Surrogate

Ceria is commonly used as a surrogate for plutonium. This is because it shares many physical and chemical characteristics. The major departure in terms of the atomic properties is that Pu can exist in (III), (IV), (V) and (VI) whereas Ce only exists in (III) and (IV). Both CeO_2 and PuO_2 are in the (IV) form so Ce may be a suitable surrogate for reductive behaviour but not for oxidative dissolution

If the results from $(U\text{-}Ce)O_2$ are to be meaningfully interpreted then the mechanistic process needs to be understood. This will be achieved by creating a model system of CeO_2 and conducting dissolution studies on it.

Methodology

The first part of the project is to understand the dissolution behaviour of ceria. This will be done by using a model system of CeO_2 thin films on a Si substrate. The films are manufactured using a process termed Physical Laser Ablation (PLA) which involves placing the substrate in the path of a vapour flume created by firing a laser at the surface of sintered target.

As shown in Figure 1 films can be manufactured which exhibit preferential orientation meaning that any results can be analysed in terms of the physical or chemical processes occurring at the surface. The behaviour of CeO_2 will be directly compared to that of PuO_2 to test the efficacy of Ce as a Pu surrogate. This will be done using mass spectrometry, weight loss, microstructural and chemical techniques and XANES.

The second part of the project is to manufacture simulant MOX $(U\text{-}Ce)O_2$ and carry out leaching tests on it using the research of CeO_2 to translate the results into predictions about the behaviour of MOX.

Conclusions

- CeO_2 thin films can be grown on (400) Si wafers with a (111) preferential orientation

- CeO_2 films can be dissolved using HCl

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