ARTICLE IN PRESS

Journal of Nuclear Materials xxx (2016) 1–7

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

The effect of fission-energy Xe ion irradiation on the structural integrity and dissolution of the CeO_2 matrix

A.J. Popel [a, b, *], S. Le Solliec [a], G.I. Lampronti [a], J. Day [a], P.K. Petrov [c], I. Farnan [a]

[a] *Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, United Kingdom*
[b] *Department of Materials, Imperial College London, London, SW7 2AZ, United Kingdom*
[c] *Department of Materials and London Centre for Nanotechnology, Imperial College London, London, SW7 2AZ, United Kingdom*

HIGHLIGHTS

- Ion irradiation induced microstructural rearrangements in CeO_2 thin films.
- Ion irradiation reduced aqueous durability of bulk and thin film CeO_2 samples.
- Secondary phases observed from dissolution of irradiated CeO_2 films in di-water.

ARTICLE INFO

Article history:
Received 14 July 2016
Received in revised form
6 September 2016
Accepted 26 October 2016
Available online xxx

Keywords:
CeO_2
Thin films
Ion irradiation
Radiation damage
Dissolution
Secondary phases

ABSTRACT

This work considers the effect of fission fragment damage on the structural integrity and dissolution of the CeO_2 matrix in water, as a simulant for the UO_2 matrix of spent nuclear fuel. For this purpose, thin films of CeO_2 on Si substrates were produced and irradiated by 92 MeV $^{129}Xe^{23+}$ ions to a fluence of 4.8×10^{15} ions/cm^2 to simulate fission damage that occurs within nuclear fuels along with bulk CeO_2 samples. The irradiated and unirradiated samples were characterised and a static batch dissolution experiment was conducted to study the effect of the induced irradiation damage on dissolution of the CeO_2 matrix. Complex restructuring took place in the irradiated films and the irradiated samples showed an increase in the amount of dissolved cerium, as compared to the corresponding unirradiated samples. Secondary phases were also observed on the surface of the irradiated CeO_2 films after the dissolution experiment.

1. Introduction

Cerium dioxide, CeO_2, is widely used as a non-radioactive structural analogue to UO_2 to study its dissolution [1–9] and the effect of radiation damage on chemical [10–13] and structural [14–22] stability. This material is also proposed as a possible component in inert matrix fuels or as part of high-level nuclear waste forms.

The use of CeO_2 is justified by the facts that it has the same Fm-3m fluorite type structure with a similar lattice parameter and cation radius as to UO_2 (Table 1) and is considered to be the most appropriate inactive analogue which can serve to gain experience to further work on UO_2.

However, there are important differences that should be remembered. Uranium is an actinide and has six valence electrons, whereas Ce is a lanthanide and has only four valence electrons. Although, there are some similarities in chemical behaviour between actinides and lanthanides, there are no ideal chemical analogues among lanthanides for Th, Pa, U, Pu and Np [27]. Therefore, it is reasonable to expect that chemical behaviour of UO_2 and CeO_2 will be different. The surface of uranium dioxide tends to oxidise in air to UO_{2+x} $(x \leq 1)$ [28], implying that some of U^{4+} converts to U^{5+} and U^{6+}. In contrast, in CeO_2 under air atmosphere trace amount of Ce^{3+} tends to be present [1], leading to a CeO_{2-x} composition. Unfortunately, the literature review did not reveal any information on dissolution mechanism of CeO_2 in water, but it is widely accepted that CeO_2 dissolves via reduction of Ce^{4+} to Ce^{3+} [48] under air atmosphere, whereas UO_2 dissolves via oxidation of U^{4+} to U^{6+} [29,30]. Work by Ohno et al. [13], Iwase et al. [12] and Kumar

---

[*] Corresponding author. Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, United Kingdom.
E-mail address: apopel@cantab.net (A.J. Popel).

http://dx.doi.org/10.1016/j.jnucmat.2016.10.046

Please cite this article in press as: A.J. Popel, et al., The effect of fission-energy Xe ion irradiation on the structural integrity and dissolution of the CeO_2 matrix, Journal of Nuclear Materials (2016), http://dx.doi.org/10.1016/j.jnucmat.2016.10.046

Table 1
Summary of lattice type, lattice parameter and cation radii for UO_2 and CeO_2.

Parameter	UO_2	CeO_2
Lattice type [23]	Fm-3m fluorite structure	Fm-3m fluorite structure
Lattice parameter (Å)	5.469 [24]	5.411 [25]
Crystal cation radius, r_{cr} (Å) [26]	1.14	1.11

et al. [10] showed that ion irradiation of CeO_2 results in an increased proportion of Ce^{3+} ions, leading to CeO_{2-x}, whereas modelling work by Kinoshita et al. [11] showed that the fission tracks in UO_2 can cause several meta-stable configurations for hyper-stoichiometric defect structures of UO_{2+x}. In addition, work by Sonoda et al. [31] showed that the diameter of ion tracks in UO_2 is much less sensitive to the electronic stopping values than in CeO_2, which indicates that UO_2 has a higher kinetic recovery of the radiation damage than CeO_2. Weber [32] reported that UO_2 has a better recovery of the radiation damage than CeO_2: it was observed that UO_2 irradiated by alpha particles showed 12% recovery of the lattice parameter compared to 10% recovery for CeO_2 following almost two years of post-irradiation storage at room temperature. In addition, the thermal recovery study showed that complete recovery of the lattice parameter was observed by 500 °C for UO_2 and by 700 °C for CeO_2.

Electrical properties of UO_2 and CeO_2 are also different. Stoichiometric UO_2 is a Mott-Hubbard insulator that converts to a p-type semiconductor UO_{2+x} due to oxygen incorporation during oxidation in air [33]. Close to stoichiometric UO_2 has the electrical conductivity values in the range 10^{-3}–10^{-4} S/cm at room temperature [34]. Stoichiometric CeO_2 is a dielectric [35] and tends to convert into CeO_{2-x} in air that is an oxygen deficient n-type semiconductor [36]. Polycrystalline thin film CeO_2 with close to stoichiometric ratio of Ce to O has the electrical conductivity values ~10^{-10} S/cm at room temperature [37].

All these differences question the suitability of using CeO_2 as an UO_2 analogue. To explore this subject further, experimental work with CeO_2 samples was conducted and the obtained results were compared with the similar work on UO_2 samples by Matzke [38]. Matzke [38] considered the effect of radiation damage on dissolution of the UO_2 matrix in water by irradiating UO_2 and UO_2-based simfuel samples with Kr and Rb ions of 40 and 45 keV energy, respectively, to induce radiation damage. This experiment showed that the leach rate of the irradiated samples increased by more than an order of magnitude.

In the current study, we produced thin films of CeO_2 on Si substrates and irradiated with 92 MeV $^{129}Xe^{23+}$ ions to a fluence of 4.8×10^{15} ions/cm^2 along with bulk CeO_2 samples. The irradiated and as-produced films were analysed for comparison using SEM (Scanning Electron Microscopy) and XPS (X-ray Photoelectron Spectroscopy) techniques. The results obtained from the XPS study will be published elsewhere. XRD (X-ray Diffraction) and EPMA (Electron Probe Microanalysis) techniques were used to assess the quality of the as-produced and as-supplied samples. A static batch dissolution experiment was conducted under an air atmosphere. Cerium concentration in the levied solutions was measured using ICP-MS (Inductively Coupled Plasma Mass Spectrometry). The samples after the dissolution experiment were characterised using SEM techniques.

2. Experimental details

2.1. Sample production

The bulk samples of CeO_2 were obtained from Sigma-Aldrich in the form of fused pieces 3–6 mm in size and 99.9% purity on trace metal basis, as claimed by the supplier.

The CeO_2 thin films were grown by pulsed laser deposition (PLD) in a Neocera PLD system with a Lambda Physik KrF laser ($\lambda = 248$ nm) with pulse duration of 50 ns on three (001) oriented p-doped Si substrates with dimensions 10 × 10 × 0.5 mm, secured by silver paste onto the stainless-steel resistive heater at Imperial College London. The target for the PLD system was in-house made from CeO_2 powder (Sigma Aldrich, 99.9% purity, < 5 μm grain size). X-ray diffraction was used to confirm that there was no change in structure from powder to pellet, both presenting a unit cell size a of 5.41 Å. Thin films were deposited from 20 mm diameter stoichometric CeO_2 target in an oxygen pressure of 100 mTorr. The substrate temperature ($T_s = 800$ K) during deposition was controlled using a thermocouple embedded in the heater. The energy density of the laser spot (2×10 mm^2) was 1.5 J/cm^2. From the sample thickness measured using a Dektak 11A, the film growth rate was estimated to be approximately 0.05 nm/pulse. The total number of pulses was 5000 with a repetition rate of 8 Hz. Once the ablation was over, the samples were then cooled down at a rate of 10 °C/min in an oxygen rich environment (760 Torr). The intention was to produce single crystal CeO_2 films in the (111) orientation to utilise the advantages that these samples can offer: idealised simplified system with one crystallographic orientation without grain boundaries and flat surface.

The thin films of CeO_2 were nominally of the same thickness, as they were deposited by the same number of laser pulses, the three samples produced had different colours. This is an indication that the thin films may have had different thicknesses [49].

2.2. Sample irradiation

To simulate the damage produced by fission fragments in nuclear fuel, the samples were irradiated with 92 MeV energy $^{129}Xe^{23+}$ ions to a fluence of 4.8×10^{15} ions/cm^2 on the IRRSUD beamline at the GANIL accelerator, Caen, France [50]. The beamline base vacuum was 6×10^{-7} mbar during the irradiation. The flux was kept at ca. 1.3×10^{10} ions/(cm^2 s) which caused heating of the samples to a temperature not exceeding 150 °C. The temporal structure of the ion beam was 1 ns ion pulse every 100 ns and the beam was swept across the surface of the samples with a frequency of 400 Hz in the horizontal and 4 Hz in the vertical direction to ensure homogenous irradiation. The samples were allowed to cool down to ambient temperature (~19 °C) before the beamline was brought to atmospheric pressure using nitrogen gas to minimise surface oxidation of the samples.

According to the SRIM-2013.00 software [39], the expected nuclear and electronic stopping, dE/dx, for 92 MeV Xe ions in CeO_2 is 0.2 and 20.9 keV/nm, respectively, and the projected ion range is ~7.5 μm. A CeO_2 density value of 7.13 g/cm^3, provided by Sigma-Aldrich for the bulk samples, was assumed in the SRIM calculation. The SRIM results indicate that the Xe ions completely penetrate the CeO_2 thin films (250 nm max) and the electronic stopping regime dominates the dissipation of ion energy throughout the entire film. The Xe ions stop in the substrate at a depth of ~13.5 μm beneath the sample's surface.

Please cite this article in press as: A.J. Popel, et al., The effect of fission-energy Xe ion irradiation on the structural integrity and dissolution of the CeO_2 matrix, Journal of Nuclear Materials (2016), http://dx.doi.org/10.1016/j.jnucmat.2016.10.046