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Structures of UO_2 and PuO_2 surfaces with hydroxide coverage

Averyl H.H. Tan [a], Robin W. Grimes [a,*], Scott Owens [b]

[a] Department of Materials, Imperial College, Prince Consort Road, London SW7 2BP, UK
[b] BNFL, NSTS, Hinton House, Risley, Warrington, Cheshire WA3 6AS, UK

Abstract

Atomic scale computer simulation is used to predict the energies and structures associated with surface hydroxide groups on the (1 0 0), (1 1 0) and (1 1 1) surfaces of UO_2 and PuO_2. The (1 0 0) surface is of particular interest since it is dipolar and therefore must be stabilised by a series of surface defects. Two different (1 0 0) defect terminations are considered, one a conventional series of surface layer defects, the other a partial reconstruction with (1 1 1) like facets. The latter is the most stable termination in the absence of hydroxide. In the presence of hydroxide this preference is reversed.

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1. Introduction

Uranium dioxide powder (UO_2) is the material most commonly used to manufacture commercial thermal reactor fuel [1]. Blends of UO_2 and plutonium oxide (PuO_2) powders are used to fabricate mixed oxide fuel [1]. In both cases the powders are hot pressed and sintered into pellets which are then assembled into fuel pins. The sintering behaviour of the powder is dependent on particle morphology. In a previous study [2], it was shown that for UO_2 the relative stability of the (1 0 0), (1 1 0) and (1 1 1) low index planes could be changed (and hence particle shape modified) if they were partially covered by dissociated water (hydroxide groups). In particular, the (1 0 0) dipolar surface was stabilised to such a degree that once it was approximately half covered by hydroxide groups, it became the dominant surface in an equilibrium crystallite morphology (even though the (1 1 1) surface was also stabilised by hydroxide coverage). Conversely, when dry, the (1 1 1) surface was considerably more stable than the (1 0 0) surface [2].

Water adsorption onto UO_2 and PuO_2 surfaces has also been the subject of experimental attention [3,4]. In particular, a value of 1.79 eV per H_2O (corresponding to a temperature of 650 K) for the recombination of hydroxide on PuO_2 leading to water desorption has been determined [3]. Unfortunately this was not attributed to a specific surface. Water desorption from a stoichiometric UO_2 (1 1 1) surface has also been studied [4]. In this case, two peaks for desorption were observed, one at 400 K and the other at 530 K (i.e. at lower temperatures than for the general PuO_2 desorption).

When perfectly cleaved, the (1 0 0) surface possesses a dipole in the direction of the surface normal; this is responsible for the complex and interesting behaviour of this surface. The dipole is removed by the formation of surface defects [5]. For UO_2, oxygen vacancies provide the lowest energy surface [6]. In this case, the

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[*] Corresponding author. Tel.: +44 20759 46730; fax: +44 20758 43194.
E-mail address: r.grimes@imperial.ac.uk (R.W. Grimes).

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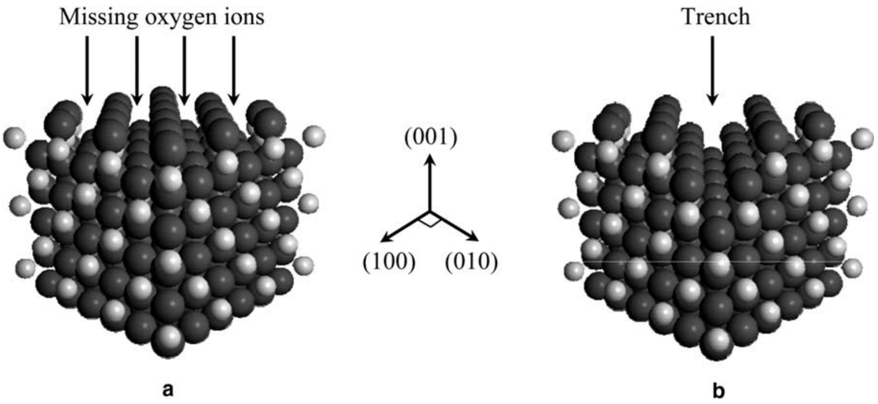

Fig. 1. The UO_2 (1 0 0) surface, (a) the 'A' configuration, (b) the trench configuration. Surface as a function of hydroxide coverage: dry (0%), 50% of possible sites and 100%.

simulation proceeds by removing half the surface oxygen ions and placing them at the bottom of the simulation block. However, there are numerous ways in which the oxygen vacancies can be arranged on the surface [6]. Of these, the planar 'A' configuration, which consists of rows of missing surface oxygen ions (vacancies), is the most stable [7] (see Fig. 1(a)). Nevertheless, recently an alternative partially reconstructed configuration has been suggested, prompted by an analysis of experimental data (low energy electron diffraction and scanning tunnelling microscope) [8]. This consists of an array of trench like grooves in the (1 0 0) surface, oriented in the [1 1 0] direction and bounded by $(\bar{1}11)$ and $(1\bar{1}1)$ facets (see Fig. 1(b)).

The aim of this study is to investigate hydroxide coverage on the low index faces of UO_2 and PuO_2 using atomic scale computer simulation techniques. In particular, the effect on the planar A and trench configurations of the (1 0 0) surface are considered.

2. Methodology

These surface simulations were performed using the code MARVIN [9]. This uses a two dimensional (2D) periodic boundary condition so that a block of ions is repeated throughout space in the *xy* plane. Here the repeat block consisted of either 2 × 2 × 12 or 3 × 3 × 12 fluorite unit cells. The total energy of the block is computed assuming pair potentials act between ions. The potential includes long range Coulomb (via a 2D Ewald technique) and short range parameterised terms. For UO_2 the parameters were taken from previous work [6,7] but a new set were derived for PuO_2 (see Table 1).

The ions in the upper half of the repeat block are relaxed using energy minimisation while those in the lower half are held fixed at their perfect lattice positions [9].

Table 1
Buckingham potential short range parameters (cut-off 14 Å) for PuO_2 calculations

Ion pair	A (eV)	ρ (Å)	C (eV Å^6)
O^{2-}–Pu^{4+}	1762.84	0.3542	11.48
$O^{1.4-}$–Pu^{4+}	1817.67	0.3388	11.48

The relaxed total energies can be used to determine the energy to cleave a perfect crystal along a specific plane (i.e. the surface energy, γ), using the equation

$$\gamma = \frac{E_{\mathrm{surf}} - E_{\mathrm{bulk}}}{A}, \tag{1}$$

where E_{surf} is the excess energy of the surface ions compared to the same number of bulk ions, E_{bulk}, and A is the area of the new surface formed.

To model hydroxylation of the surface, we calculate the energy to dissociate a water (H_2O) molecule into OH^- and H^+; we then place the OH^- at an unoccupied oxygen surface site and finally protonate a surface O^{2-} ion to form a second surface OH^-. The addition of water molecules is repeated until the desired coverage is reached. This surface is then allowed to relax via energy minimisation. The energies of hydroxylated surfaces are calculated using an energy cycle that includes experimental data for processes such as molecular water dissociation and has been used previously for hydroxylation studies of t-ZrO_2 and UO_2 [2,10]. The cycle allows us to determine the hydroxylated surface energy, γ_{hyd}, via

$$\gamma_{\mathrm{hyd}} = \frac{\{U_{\mathrm{surf}}(\mathrm{hyd}) - U_{\mathrm{bulk}}\} + nE_{\mathrm{corr}}}{A}, \tag{2}$$

where U_{surf} is the total energy of the surface block with n adsorbed water molecules and E_{corr} is the sum of the experimental terms including molecular water dissociation. The energy of hydroxylation (the energy gained per water molecule at a specific coverage by hydroxylating the surface), E_{hyd}, is defined by

$$E_{\text{hyd}} = \left[\frac{U_{\text{surf}}(\text{hyd}) - U_{\text{surf}}(\text{dry})}{n}\right] + E_{\text{corr}}. \tag{3}$$

3. Results and discussion

From the results for UO_2 in Table 2 (column 2) it is clear that, in the absence of hydroxide (i.e. dry) the trench configuration provides a lower energy termination for the (1 0 0) surface than the planar (1 0 0)A configuration [7]. Here we report that the same holds true for PuO_2 (also Table 2). The (1 1 1) surface however, remains sufficiently more stable than (1 0 0), for both UO_2 and PuO_2, that the crystal morphology will be dominated by (1 1 1). The resulting equilibrium morphologies are therefore octahedra.

Previous modelling work on UO_2 [2] suggests that small amounts of surface hydroxide will be incorporated onto the (1 0 0) surface in preference to other surfaces, resulting in the (1 0 0) surface becoming stabilised compared to the (1 1 1) and (1 1 0) surfaces. In that work [2], hydroxylation of planar (1 0 0) configurations were considered, but not hydroxylation of the partially reconstructed trench configuration, as is the case here (see Table 2). The results for UO_2 and PuO_2 suggest that at a 50% hydroxide coverage, the trench configuration remains more stable than the planar A configuration (Table 2, column 3). However, once all possible sites are occupied by hydroxide (i.e. 100% occupation) the A configuration is more stable than the trench configuration. It is possible to understand how the A configuration becomes more stable by considering the structure of the trench. Essentially it consists of planar (1 0 0) areas bisected by small (1 1 1) facets. These two surface types occur roughly in equal proportions. The hydroxide groups preferentially occupy the planar sites up to approximately an overall 50% coverage. Fig. 2 shows the hydroxylation energy of PuO_2 as a function of site coverage: the hydroxylation energy for the trench configuration approximately follows that of the (1 0 0)A configuration up to 50% coverage. Beyond this, the hydroxide groups occupy the (1 1 1) facet sites and the slope of the hydroxylation energy follows the trend of (1 1 1) surface hydroxylation, which is less favourable then that for the (1 0 0)A surface. The hydroxylation energies in Fig. 2 can also be compared to the experimental value for hydroxide recombination and desorption from a PuO_2 surface [7]. This value, 1.79 eV, falls in the middle of the predicted values (Fig. 2) as seems appropriate given that the experimental value is for a general surface.

Table 2
Calculated surface energies of (1 1 1), (1 1 0) and two configurations of (1 0 0) with (a) no surface hydroxide (dry), (b) 50% surface sites occupied by hydroxide and (c) all surface sites covered (100%)

	Surface energy, γ (J/m^2)		
	Dry	50%	100%
UO_2			
(1 1 1)	1.29	0.85	1.48
(1 1 0)	2.04	1.21	0.83
(1 0 0)A	2.85	1.54	0.45
Trench	2.45	1.18	1.33
PuO_2			
(1 1 1)	1.39	1.04	1.69
(1 1 0)	2.20	1.40	1.05
(1 0 0)A	2.92	1.72	0.69
Trench	2.55	1.44	1.36

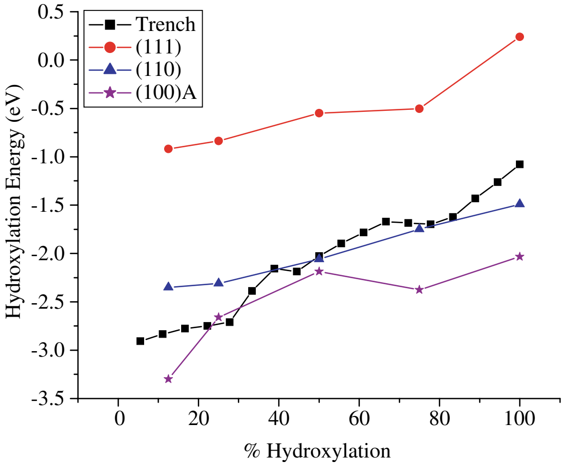

Fig. 2. Hydroxylation energy of PuO_2 as a function of surface hydroxide coverage.

Perhaps as significant as the relative planar and trench (1 0 0) prediction is that the 100% covered planar configuration is more stable than any other surfaces at any other hydroxide coverage (see Table 2). Consequently, if sufficient water is available to be incorporated onto surfaces, the equilibrium morphologies of UO_2 and PuO_2 will be dominated by the planar (1 0 0) surfaces and a cubic morphology results.

4. Conclusion

For the dry surfaces of both UO_2 and PuO_2, the (1 1 1) surface is more stable then either (1 1 0) or (1 0 0). Once covered with hydroxide groups, however, the (1 0 0) surface becomes the most stable. In terms of particle morphology predictions (which depend on both surface energy and the surface normal vector length

[2,6]) this means that the (1 0 0) surface becomes significant at a 50% hydroxide coverage and dominant at 100%.

In the absence of hydroxide, the most stable (1 0 0) surface structure consists of parallel rows of truncated (1 1 1) facetted trenches [8]. In the presence of hydroxide groups, the planar (1 0 0)A configuration is greatly stabilised and once 100% coverage is achieved it is more stable than the trench configuration. The rates at which a previously dry trench configuration can restructure to become planar once hydroxylated, or a previously planar hydroxylated surface can restructure to a trench once dry is not yet known.

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