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Segregation of Fission Products to Surfaces of UO$_2$

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ABSTRACT

In order to predict the release rates of fission products from UO$_2$ nuclear fuel, it is necessary to determine the energetics associated with their segregation from the bulk to surfaces. Here segregation is determined by calculating the total energy of a simulation repeat unit which includes a fission product, as a function of the distance of the fission product from the surface. We have investigated the possibility that specific fission products segregate preferentially to certain surfaces. In particular, Ce^{4+} and Zr^{4+} segregate to the (100) surface, while Ba^{2+} and Sr^{2+} segregate to the (111) surface. Two issues make these calculations more complex. First, charged defects need to be compensated by oxygen vacancies. For example, divalent Ba^{2+} and Sr^{2+} substituting on uranium sites are compensated by a single oxygen vacancy. Second, certain surfaces, such as the (100), are inherently unstable, but can be stabilized by oxygen vacancies. Arrangements of these surface defects lead to complex surface structures that effect segregation energetics.

INTRODUCTION

Our motivation for this study is to better predict the release of fission products from nuclear fuel, if the fuel cladding is breached. There have been extensive studies, both theoretical and experimental, which have attempted to initially categorize fission products based upon their chemistry within the fuel matrix [1,2] and later studies which concerned themselves with the diffusion of fission products and the distribution of fission products within a single grain [3-5]. An important aspect of this problem is the segregation of fission products to specific surfaces of UO$_2$. Such calculations require an atomistic approach which, to our knowledge, has not been applied to this problem previously. More specifically, we calculate the segregation of fission products to the (111) and (100) surfaces. It will be shown that the segregation of fission products is surface dependent. Other aspects important to fission product segregation (such as defect cluster orientation) will also become evident.

## METHODOLOGY

Fission segregation is determined using atomistic simulation techniques based on energy minimisation using pair potentials. In this work, the computational codes CASCADE [6] and MARVIN [7] are employed. CASCADE is used to determine bulk perfect lattice energies, which are subsequently incorporated into MARVIN, which simulates surfaces and interfaces.

The energies calculated by the different codes are comparable because they use the same short-range potential description of forces and both codes use energy minimisation techniques.

MARVIN constructs a surface by periodically repeating a characteristic unit block. Therefore, we must consider a characteristic region large enough so that the results are not dominated by non-physical defect-defect interactions horizontal to the surface. However, the larger the region size, the more computationally taxing the calculation. Therefore a compromise must be reached between computation time and simulation accuracy, with a distinct bias towards simulation accuracy. The results in this paper were obtained using either region sizes of 2x2x6 full unit cells in the x, y and z direction respectively, or larger 3x3x6 unit cells. Segregation trends are established by introducing a fission product into the UO$_2$ lattice. This defect is systematically moved layer by layer, from the surface to the bulk, calculating the total energy at each step. The total energy is then considered as a function of distance from surface.

The (110) surface is a neutral Type 1 surface (as defined by Tasker [8]), consisting of alternating charge neutral layers of both anions and cations. The (111) is a Type 2 surface, as it consists of alternating charged layers of anions cations, but arranged symmetrically so that there is no dipole moment perpendicular to the surface. The (100) surface is a Type 3 surface, which consists of alternating layers of anions and cations, which can not be arranged in such a way to neutralize the dipole. In order to create a physically stable (100) surface, a series of oxygen vacancies must be formed on the anion terminated surface such that only half of the oxygen sites are occupied. Abramowski et al. [9] have identified three low energy configurations of oxygen atoms on the defective (100) surface, which are used in this study, see Fig 1.
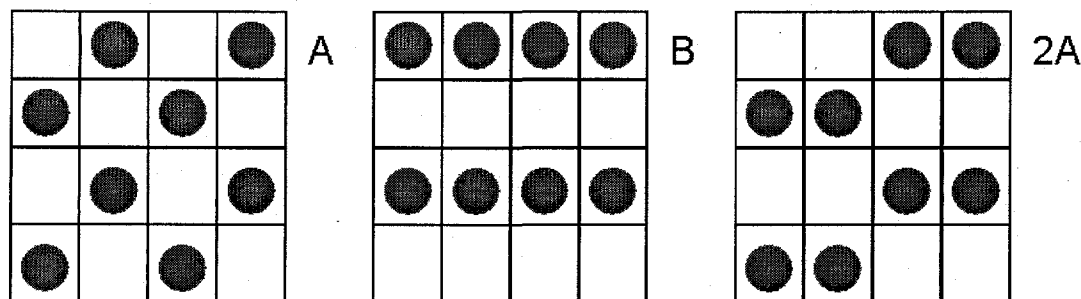

Figure 1: *The three anion terminated surfaces used in this study, where each dot represents a surface oxygen atom and each intersection represents a uranium atom a layer beneath.*

The fission products Ce^{4+}, Zr^{4+}, Ba^{2+} and Sr^{2+} are considered. The tetra-valent fission products (Ce^{4+} and Zr^{4+}) substitute for U^{4+}, forming charge neutral defects. The divalent fission products (Ba^{2+} and Sr^{2+}) are similarly considered to substitute for U^{4+} [10] resulting in a charged defect which must be compensated by an oxygen vacancy. The resulting defect cluster can have several configurations with respect to the different surfaces of UO$_2$. Fig. 2 shows the four possible configurations of the $\{(Me_U)''{:}(V_O)^{..}\}$ cluster with respect to the (111) surface.
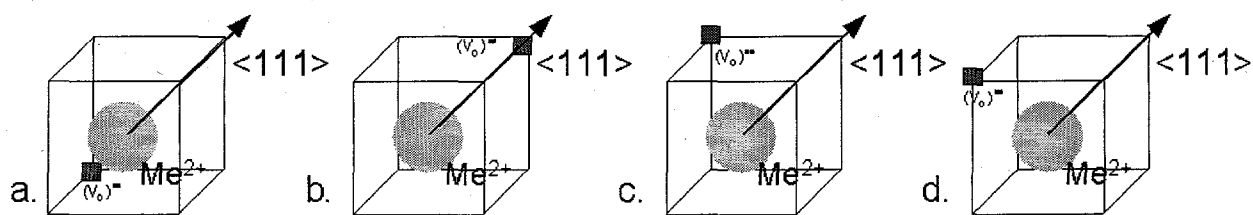
Figure 2: *The configurations of {(Me $_U$)'':(V$_O$)''} with respect to the (111) surface, where the notation, a-d, is used throughout the text.*

Fig. 3 depicts the cluster configuration with respect to the (100) surface. After examining Fig. 1, it becomes clear that the anion terminations considered can be classified by either oxygen atoms residing directly next to, or diagonally opposing one another. The left hand graphic in Fig. 3 applies to configuration A, as the anions are always diagonally opposed. The right hand graphic in Fig. 3 applies to configuration B, as the anions are always in rows. Both pictures apply to configuration 2A, as it is a hybridisation of the A and B terminations and will therefore have anions across from and diagonally opposing one another.
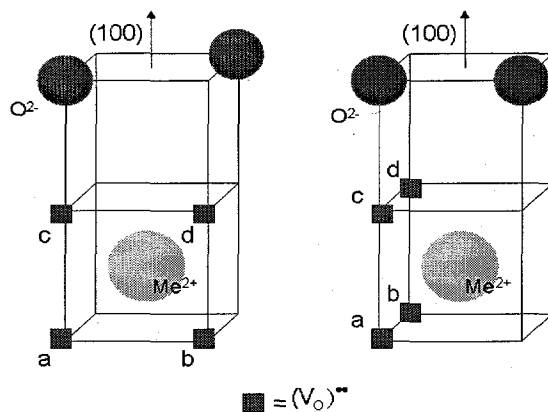

Figure 3: *The configurations of {(Me $_U$)'':(V$_O$)''} with respect to the (100) surface, where the notation, a-d, is used throughout the text.*

RESULTS

Let us define an energy E_S to be the difference between the fission product in the bulk and at the surface. Let us also define an energy E_T to be the difference between the energy of the fission product at the surface and in the lowest energy trap site. It is evident from Fig. 4, that Zr^{4+} is trapped just beneath the (111) surface, with $E_S = 0.261eV$ and $E_T = 0.352eV$. A slightly different behaviour was observed for Ce^{4+}, in that the trap site just beneath the surface is not as prounced as with Zr^{4+}, with $E_T - E_S = 0.004eV$, see Fig. 4. However, similar to the behaviour of

Zr^{4+}, Ce^{4+} does not to segregate to the (111) surface, with E_S = 0.232eV. The reason for this difference in behaviour can be attributed to the similar sizes and charge of cerium and uranium.
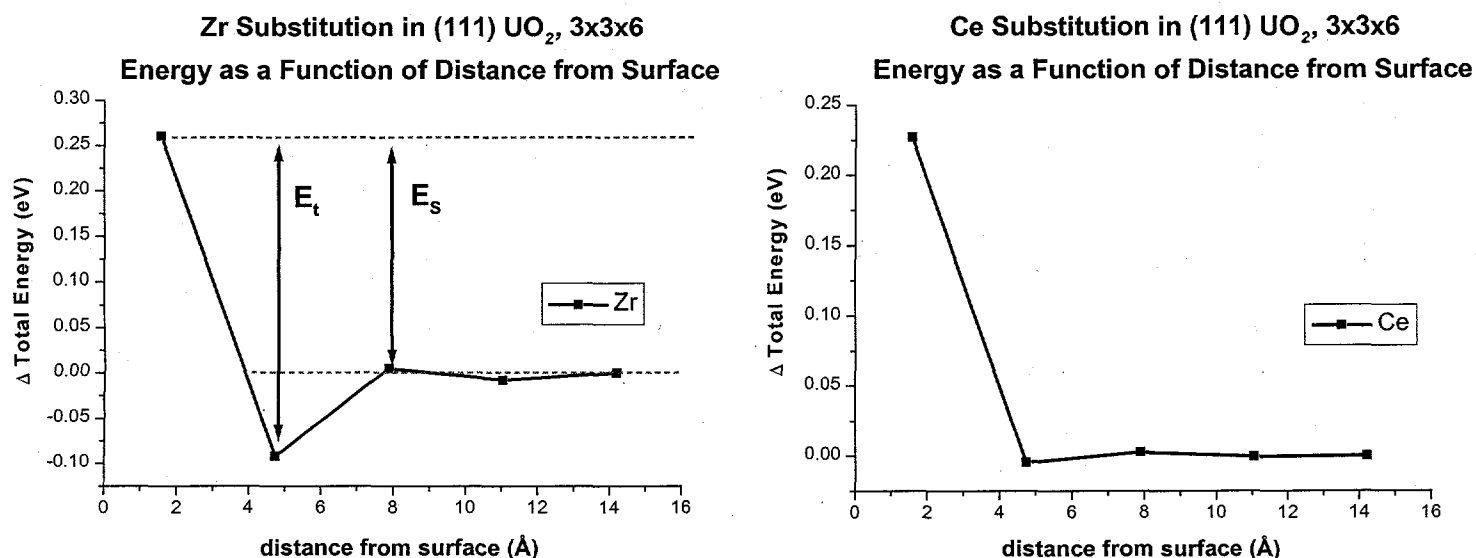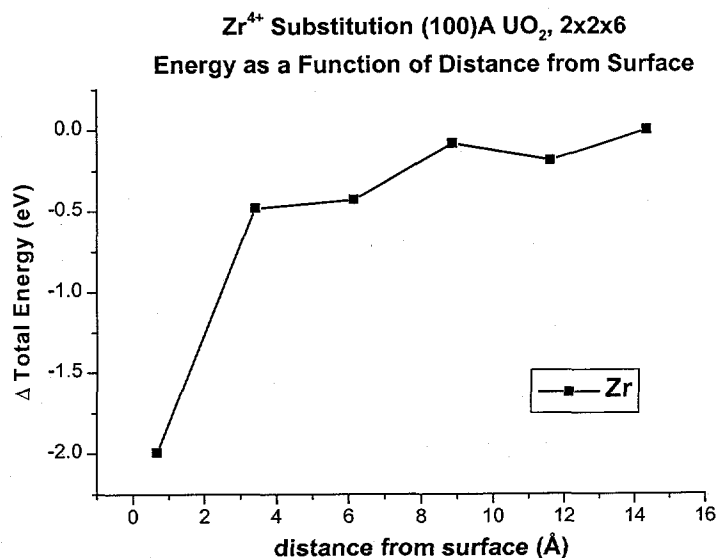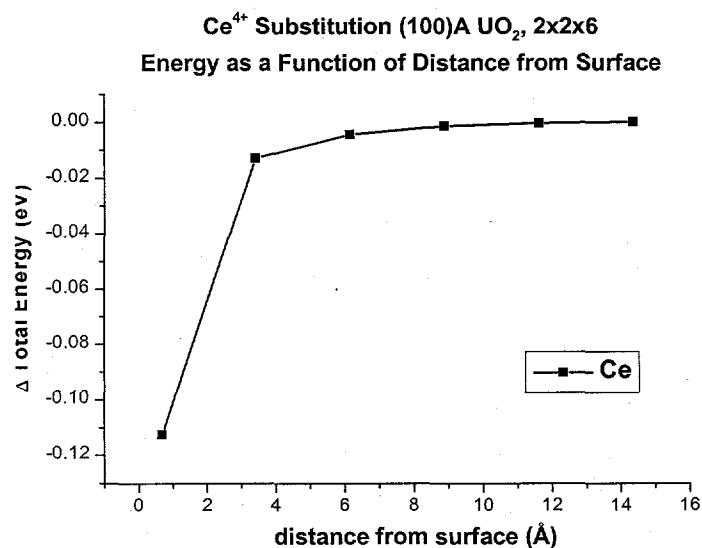

Figure 4: *The total energy of the Zr^{4+} and Ce^{4+} substitutional defects as a function of depth in a (111) UO_2 lattice, using a computational cell size of 3x3x6 unit cells.*

In Fig. 5, it is clear that there is a pronounced driving force for both Ba^{2+} and Sr^{2+} to segregate to the (111) surface of UO_2. The segregation energies for Ba^{2+} and Sr^{2+} are E_S = -2.706eV and E_S = -1.603eV respectively. Clearly, the driving force for Ba^{2+} to segregate is greater than for Sr^{2+}. Fig. 5 also shows that within the bulk (i.e. >11Å from the surface) there is no preference between the cluster configurations. Conversely, nearer to the surface, it appears that there is a cluster configuration dependence. This behaviour is a consequence of how the strain field induced by the cluster interacts with the strain field induced by the surface (i.e. a competition between the relaxation modes).

Fig. 6 predicts that Ce^{4+} and Zr^{4+} segregate to the A anion surface termination of the (100) surface. This result is the direct opposite to the trend that was predicted for the (111) surface. However, results for the other anion termination configurations (B and 2A) were similar to that observed for the (111). What this suggests is that segregation is not only a function of surface, but also a function of the particular configuration of surface defects (i.e. of oxygen termination).
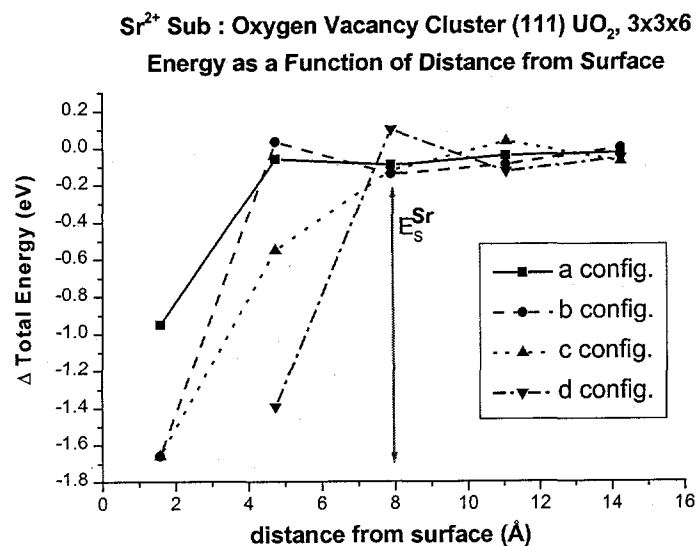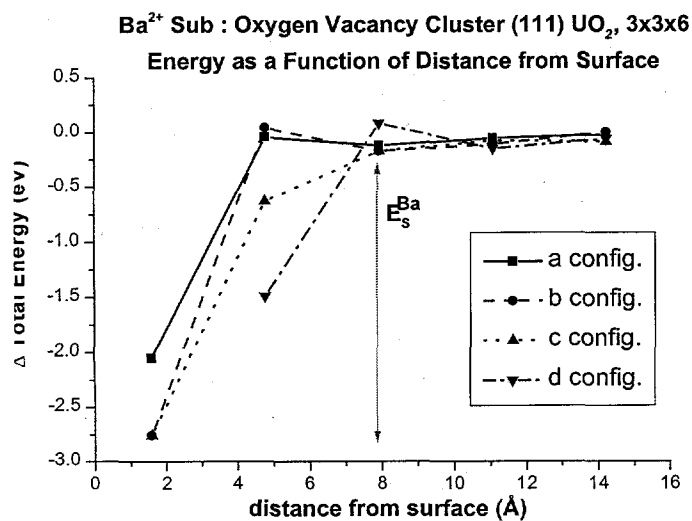
Figure 5: *The total energy of {(Me$_U$)'':(V$_O$)··} clusters as a function of depth in a (111) UO$_2$ lattice, using a computational cell size of 3x3x6 unit cells.*

Figure 6: *The total energy of the Zr^{4+} and Ce^{4+} substitutional defects as a function of depth in a (100)A UO_2 lattice, using a computational cell size of 2x2x6 unit cells.*

CONCLUSIONS

- Computer simulation calculations suggest that Ce^{4+} and Zr^{4+} show no tendency to segregate to the (111) surface and furthermore, Zr^{4+} is trapped just below this surface.

- In contrast, it was shown that Ba^{2+} and Sr^{2+} do display a tendency to segregate to the (111) surface, and segregation is a function of cluster configuration with respect to the (111) surface.

- Results for Ce^{4+} and Zr^{4+} segregation to the (100)A surface demonstrate opposite trends compared to (111) segregation. However, Ce^{4+} and Zr^{4+} segregation to the (100)B and (100)2A surfaces is similar to that for the (111) surface. Thus, segregation is not only a function of fission product species and surface, but also cluster configuration with respect to the surface (in the case of charged defects) and configuration of the terminated surface.

ACKNOWLEDGEMENTS

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