Chapter 4

Segregation of Fission Products to UO_2 Surfaces

"But we know from observation that it is only within very small distances of such a surface that any mass is sensibly affected by its vicinity, - a natural consequence of the exceedingly small sphere of sensible molecular action."

J.W. Gibbs

On the Equilibrium of Heterogeneous Substances, 1875

4.1 Introduction

Segregation of fission products to the stable low index surfaces of UO_2 has been predicted using atomistic simulation techniques. Three pairs of fission products were considered: isolvalent Ce⁴⁺ and Zr⁴⁺, divalent Ba²⁺ and Sr²⁺ and zero valent Kr^o and Xe^o. The divalent and zero valent fission products are charge compensated by oxygen vacancies. Three low index surfaces are considered: (110), (111) and (100). The (100) surface is dipolar (Type III) and therefore unstable. Thus, a series of surface defects must be incorporated to neutralize the dipole. The dependence of segregation upon specific surface type, configuration of surface defects on dipolar surfaces, defect cluster geometry and fission product chemistry is discussed.

4.2 Previous Work

4.2.1 Experimental Segregation Studies

Properties of oxide materials (e.g. strength, sinterability, conductivity, creep, etc.) are governed to a large extent by defects as well the structure and stability of surfaces and interfaces. Understanding the segregation of impurities to these surfaces and interfaces will therefore be important in controlling materials properties. Unfortunately, experiments in this area are few, attesting to the difficulty of these types of study. The seminal work of McCune and Wynblatt [167] has served as an impetus to motivate further work. They investigated the segregation of Ca^{2+} to the (100) surface of the prototypical ionic ceramic, MgO, by using low energy ion scattering spectroscopy and Auger spectroscopy to measure equilibrium surface coverage. Roshko and Kingery similarly looked at segregation of Ca^{2+} in MgO [168], but rather than to (100) surfaces, they investigated three high angle grain boundaries using scanning transmission electron microscopy. They found different segregation behaviour for Ca to the different boundaries, suggesting that grain boundary structure does have an effect on segregation.

In order to better understand the phenomenon whereby MgO beneficially affects the sintering of Al_2O_3 , Baik, Mukhopadhyay, Blakely *et al.* investigated the segregation of Mg and Ca to Al_2O_3 surfaces [63, 169, 170]. Early grain boundary experiments on MgO doped Al_2O_3 surprisingly revealed the segregation of Ca [171]. This observation was interesting considering that the concentration of Ca in the bulk was between 5 and 15 ppm. In similar surface sensitive experiments, Ca was also found [172–174]. Unfortunately, Ca has a detrimental effect on densification [175]. Nevertheless, due to these early segregation studies, Baik, Mukhopadhyay, Blakely *et al.* were forced to consider Ca as well as Mg in their experiments.

An interesting result from the work of Mukhopadhyay *et al.* is that the segregation behaviour of both Ca and Mg was different for the $(10\bar{1}0)$ prismatic plane than it was for the (0001) basal plane of Al₂O₃. The effective heat of segregation for Mg was found to be lower for the basal plane than the prismatic plane, although qualitatively similar (differing only by $\approx 0.5 \text{eV}$) [63]. Baik and White found that Ca did not segregate to the (0001) surface while there was strong segregation to the (10 $\bar{1}0$) surface [169].

4.2.2 Modelling Segregation Studies

The simulation of segregation can be considered as a progression of the early computational work of the type mentioned in Chapters 2 and 3. Much of the methodology is based exactly on the earlier bulk material and surface methodology. As mentioned in the previous section, experimental segregation studies are very difficult to perform. It then follows that simulation studies concerned with segregation can be potentially useful in providing information where equivalent experimental work would be rather challenging. Furthermore, simulations can be a valuable tool not only in predicting segregation behaviour, but also in complimenting or directing experimental work.

That said, there have been relatively few segregation simulation studies compared to equivalent studies of bulk materials or even surface structure. Nevertheless, several simulation methods for determining segregation trends have been applied. Monte Carlo techniques have been used previously in metals [176, 177], but until recently have not been used in ionic solids because of their computational intensity. Harding *et al.* have used modified, kinetic Monte Carlo techniques to investigate diffusion in grain boundaries in the ionic solids NiO and Al_2O_3 [178], but not segregation to these boundaries.

The early work of Tasker and co-workers used similar techniques as described in Chapter 2 to determine surface energetics and segregation trends in metal oxides [76, 179–181]. In the first of these studies [76], Tasker et al. combined detailed atomistic simulation techniques with simple statistical mechanics to describe Ca segregation to surfaces of MgO. Results obtained using potentials derived both empirically and by quantum mechanical calculations were in agreement with the experimental results of McCune and Wynblatt discussed previously [167]. Defect formation energies near surfaces and grain boundaries were also investigated [179, 180]. In these studies, it was found that defect formation energies vary with depth from the surface or boundary. This result suggests that the population and kinetics of defects are surface or boundary dependent. Tasker *et al.* then expanded the scope of their work by considering the segregation of Be, Mg, Ca, Ba and Ni to (001) and (110) surfaces of MgO and CaO [181]. Not only did this seminal paper investigate the concentration and segregation of defects at the surfaces of MgO and CaO, but also accounted for ensuing effects, such as facetting. It was also shown that dopants near the surfaces of MgO and CaO can have important effects on the structure and properties. An interesting review can be found in another paper by Tasker [182].

Cotter *et al.* also investigated Ba segregation in MgO, both experimentally with XPS and theoretically using atomistic simulation techniques [183]. Unfortunately, the scatter in the experimental data was too large to allow meaningful comparison with the modelling results. Cotter *et al.* also specifically assumed that the vibrational entropy of segregation was small compared with the enthalpy of segregation.

gation [183].

With a method well established to determine segregation trends to surfaces of simple oxides, more complex materials were duly investigated. Davies *et al.* investigated the segregation of various dopants to surfaces of oxides with the corundum structure [184]. In contrast to the Langmuir adsorption model, their results suggest that segregation enthalpy is coverage dependent. Their results for Ca segregation to the prismatic plane of Al_2O_3 qualitatively agree with the previously mentioned results of Baik *et al.* [169], though they noted that the results for the basal plane were not as convincing, citing the complexity of the segregation phenomenon.

A review of the work conducted at the University of Bath is provided in [185]. Not only does this paper detail the simulation of impurity segregation to surfaces of Al_2O_3 and ZrO_2 , but also discusses morphology as well as the generation of segregation paths via molecular dynamics. Of particular relevance to the work in this thesis is the study by Sayle *et al.*, which investigated the segregation of Rh^{3+} , Pd^{2+} and Pt^{2+} to the (111) and (110) surfaces of CeO_2 [186]. For Pd^{2+} and Pt^{2+} , they found preferential segregation of isolated defects as well as the formation of coherent second phases at the (111) surface.

The work of Sayle *et al.* paved the way for more recent studies, such as that of Slater *et al.* [187]. This work investigated the segregation of Sb to the (110) and (001) surfaces of SnO₂. Applications for SnO₂ include gas sensors and thin film coatings, and the conductivity of this material may be enhanced by doping with Sb or by forming oxygen vacancies. However, both Sn and Sb exhibit variable charge states, which increases the number of potential contributing defects. Slater *et al.* therefore began this study by calculating defect energies for Sb³⁺, Sb⁵⁺, Sn²⁺ and Sn⁴⁺ as well as an oxygen vacancy, and their corresponding defect clusters. Surface energies for SnO₂ were then calculated and successfully compared to the work of Mullheran and Harding [188]. Segregation energies were calculated for each defect complex by comparing bulk defect energies with those on the surface.

In attempt to improve upon the Langmuir - McLean method (LM), utilized in aforementioned studies [181, 182] to determine segregation trends, Srolovitz et al. have used the atomistic simulation type methods (LM) to describe atomic interactions and combined it with a minimization of free energy [189, 190]. Several limitations of the LM method are cited by Srolovitz *et al.* as the reason for employing free energy minimization. These limitations include: the inability to account for surface concentration, neglect of the finite extent of segregation (i.e. not just at the surface), inaccurate emphasis on solute misfit as well as the lack of accounting for vibrational contributions. The free energy minimization technique used by Scolovitz et al. combines interionic pair potentials with a local harmonic approximation of lattice dynamics [190] and a mean-field effective atom representation of solute concentrations [191]. Srolovitz et al. have used this technique to calculate the segregation of Ca^{2+} , Mn^{2+} and Sr^{2+} to the (001) and (011) surfaces of CaO, MnO and SrO. Each of these oxides was doped with Co, Fe and Ni. Despite a different approach, the results of Srolovitz were found to be in agreement with both LM and Monte Carlo methods [189]. The agreement with LM methods suggested to the authors that vibrational effects are of only limited importance in determining the segregation to free surfaces, thereby supporting the assumption of Cotter et al. [183].

4.3 Surfaces of UO₂

The three stable, lowest index surfaces of UO_2 , as defined by Miller indices, are the (110), (111) and (100). Recalling the Tasker classification of surfaces described in Chapter 1, the (110) surface is a neutral Type 1 surface and therefore has no surface normal dipole to account for. The anion terminated (111) surface has charged

individual planes though there is no dipole perpendicular to the surface (so long as the block is cut at the appropriate layer, see Section 1.3) and is therefore denoted as Type 2. The (100) surface is of the unstable Type 3 distinction. In order to create a physically stable (100) surface, a series of vacancies must be formed on the surface. In the case of cation terminated UO_2 , half of an oxygen layer is moved from the bottom of the simulated bulk, to the surface which serves to neutralize the dipole. If a surface consisting of only one unit cell is initially considered, there are two ways to configure the neutralizing oxygen ions: diagonally opposing or next to each other (see Figure 4.1 A and B). However, if a larger surface repeat unit is considered, there will be many more possible configurations of the oxygen ions than for a single unit cell. In fact, if a surface region of 2x2 unit cells is considered, to arrange the 8 oxygens in the 16 available positions, there will be =16!/8!8! (= 12,870) ways to arrange the surface oxygens. However, this number is reduced by the symmetry of the repeat block to 153 unequivalent configurations of the oxygen ions [44]. Of these 153 configurations, Abramowski [44] found those denoted as A and B to be the lowest energy surfaces, and in addition, an AB hybrid, see Figure 4.1.



Figure 4.1: The three anion terminations of the (100) UO₂ surface considered in this work, calculated to be low energy by Abramowski [44].

As mentioned above, the A and B configurations can be formed in a single unit cell repeat. However, the AB hybrid requires the larger 2x2 repeat unit. The AB

hybrid was also recently seen in MD simulations of the (100) surface of CaF_2 [192]. In this case, the (100) surface was simulated by using a single cluster of 3645 ions bounded by (111) and (100) surfaces. The (100) surface sizes were equivalent to an array of 3x3 single cells. After equilibrating for 10ns at 300K, the (100) surface consisted of an intergrowth of type A and type AB surfaces.

As the A, B and AB were found to be the lowest energy surfaces, they are the three that are considered in this segregation study. However, for segregation calculations, a 3x3 unit cell size has been employed as opposed to 2x2, in order to reduce defect - defect interactions between adjacent period boundary images. A 3x3 repeat unit clearly leads to many more surface configurations than the 153 considered by Abramowski. To be sure, the number of ways to configure the surface oxygen ions in a 3x3 cell size has not yet been calculated (although, without symmetry the number of configurations is greater than $9x10^9$). It is an assumption of this work that the three (100) surface configurations utilized remain the low energy surfaces with the larger surface repeat unit size. However, when the AB surface consisting of 3x3 cells is repeated, rather than a strictly AB surface (as would be the case if the repeat cell was 2x2), an intergrowth of AB and B is obtained. This intergrowth is analogous to that observed in CaF₂ and is therefore considered in this work.

Previous surface studies have been concerned with equilibrium morphology and stability of various crystallites. Those of particular relevance were conducted on stoichiometric CeO₂ [137] and UO₂ [45]. Both of these oxides crystallize in the fluorite structure, as mentioned in Chapter 1. These studies are similar in methodology (atomistic simulation as described in Chapter 2) and employ the same computational code (MARVIN) as used in the work presented in this thesis. Both previous studies predict that the equilibrium morphologies of CeO₂ and UO₂ are dominated by the (111) face. However, if thermodynamic equilibrium is not reached, and morphology is instead governed by growth (i.e. kinetics), other surfaces were shown to be of importance (e.g. (100)).

STM experiments which have been conducted on all three of the UO₂ surfaces considered in this work [193–196] show that the structure of UO₂ surfaces can be quite complex, and that it is not necessarily accurate to assume that a simple low energy (111) surface is always sufficient. Temperature and stoichiometry can have effects on the surface termination. For example, the (110) surface of stoichiometric UO₂ has been shown to be slightly defective, with missing rows of surface atoms along the [110] direction [196]. However, the (110) surface of hyper-stoichiometric UO_{2+x} has been shown to be different than the stoichiometric surface. Muggelberg *et al.* suggest the formation of dimer pairs on the hyper-stoichiometric (110) surface to be the initial stages of U-O superstructure formation, as described by Campbell *et al.* [197]. The formation of this superstructure is suggested to be a function of temperature and extent of non-stoichiometry. Nevertheless, in the STM experiments, it was not clear if equilibrium had been established.

It should be noted that in this thesis, a stoichiometric material is assumed, and as such, the results are not applicable to non-stoichiometric $UO_{2\pm x}$, though it is noted that the investigation of the superstructure surfaces inherent to non-stoichiometric $UO_{2\pm x}$ as described above is worthwhile.

4.4 Methodology

In this work, three types of segregating species are investigated, categorized by their charge state. Ce⁴⁺ and Zr⁴⁺ are of the same charge state as U⁴⁺, and therefore simply substitute for U⁴⁺. This is in concert with previous calculations [36], which have determined the low energy solution site for Ce⁴⁺ and Zr⁴⁺ in stoichiometric UO₂ to be a uranium vacancy. Ba²⁺ and Sr²⁺ are also considered to substitute for

 U^{4+} , but since they also substitute at uranium sites, the dissimilar charge needs to be compensated by an oxygen vacancy. Again, when compared to previous solution site calculations, the uranium/oxygen divacancy is a competitive site. Unfortunately, since it uses a supercell repeat methodology, MARVIN is unable to account for charged defects, and therefore, it was not possible to consider isolated charged solution sites. Finally, zero-valent Kr^o and Xe^o substitute for U⁴⁺, but need to be charge compensated by two oxygen vacancies. As discussed in Chapter 3, the neutral tri-vacancy is the low energy solution site for these fission products.

Since these calculations are not dynamical in nature, it is necessary to develop a strategy to determine segregation trends from available data. This study investigates the effect of surface relaxation on segregation. As such, a characteristic repeat unit is defined. To determine segregation trends, each of these fission product defects is introduced into the bulk, where a calculation is performed to determine its energy. The defect is then systematically moved stepwise to the surface, where a calculation is performed at each layer (see Figure 4.2). These energies are then compared to one another and plotted as a function of depth. By means of relative energies, this approximately describes the chemical potential, which is the driving force for segregation. It is important to note that the energies used to determine and discuss segregation trends are *relative*.



Figure 4.2: A 2x2x6 repeat unit of the anion terminated (100)AB surface of UO_2 , where the white atom represents the segregating species.

It is also important to note that a concern here, and indeed with any atomistic calculation, is the size of the simulation cell. For example, Figure 4.2 depicts a simulation cell of 2x2x6 unit cells in the x, y and z directions respectively. Initially this work began using a simulation cell of 1x1x6 unit cells in size. Unfortunately, this was far too restrictive, giving rise to horizontal, unphysical defect-defect interactions. This defect-defect interaction is evident in in Figure 4.3(a). In this plot, there is a pronounced gap between the sets of data labelled a and d config., and the sets of data labelled b and c config. The meaning of each data label will be discussed in Section 4.4.1.



(c) 3x3x9

Figure 4.3: The calculated relative energies of $\{(Ba_U)'':(V_O)''\}$ as a function of depth from the (111) surface using 1x1x6, 2x2x6 and 3x3x9 simulation cells respectively. As the simulation cell increases in size, the unphysical defect - defect interaction is reduced.

To reduce the defect-defect interactions, larger simulation cells were used. The 2x2x6 simulation cell in Figure 4.3(b) was also found to be unsatisfactorily small. Therefore, a 3x3x9 unit cell simulation block was employed, see Figure 4.3(c). There are several reasons to use a simulation block of this size. First, some evidence

of horizontal defect - defect interaction remains in Figure 4.3(b) (though greatly reduced). Second, in some results (to follow), cluster configuration effects were still evident at depths greater than 6 unit cells (see next section). Results for each of the two larger cell sizes are compared to the 1x1x6 cell size in Figure 4.3. It is clear that by using a repeat cell of 3x3x9 unit cells, the total defect energies have converged with respect to cell size. The results which follow are denoted with the simulation cell size that was used.

4.4.1 Orientation of Fission Product Defect Clusters

In Chapter 3, the concept of low energy solution site was introduced in regard to defect clusters. For example, in these segregation calculations Ba and Sr are considered as a constituent of a defect cluster which also consists of a single oxygen vacancy and single uranium vacancy (where the divalent ion resides). This cluster is configured such that the oxygen vacancy is in a nearest neighbour position with respect to the Ba or Sr atom, as it was calculated to have a lower energy than other defect clusters [36]. This preference was determined by calculating the binding energy of the cluster, where binding energy is defined as:

$$BE_{\text{cluster}} = \left[\sum_{\text{components}} E_{\text{defect}}\right] - E_{\text{cluster}}$$
 (4.1)

Binding energies are calculated by systematically moving the oxygen vacancy in question (namely, in Kröger-Vink notation $(V_O)^{"}$) away from the Ba or Sr at the uranium site (i.e. $\{(Me_U)^{"}\}$) one atomic position at a time and calculating the defect energy at each step. A positive binding energy indicates a preference for the defects to form a cluster rather than to remain isolated. From Figure 4.4, it is clear that the nearest neighbour configuration is preferred.



Cluster Binding Energy as a Function of Separation

Figure 4.4: The binding energy of the $\{(Me_U)'':(V_O)''\}$ cluster plotted as a function of separation.

An interesting side note about Figure 4.4 is that the binding energy at 7Å begins to follow the Coulombic trend line, as is to be expected. However, at a separation of ≈ 12 Å, the binding energy deviates from the Coulombic trend. This drop in energy can be accounted for by a defect nearing the Region I - Region II boundary. If Region I was enlarged, it is expected that the binding energy would continue to follow the Coulombic trend. What is also interesting from Figure 4.4, is that even at a separation of ≈ 13.5 Å, the binding energy is still $\approx 25\%$ of the maximum binding energy at a separation of ≈ 2 Å. This behaviour suggests that at realistic defect concentrations (i.e. above the dilute limit, in Figure 4.4 at 13.5Å this corresponds to just below 2%), defects can only be "*isolated*" to a certain extent.

For the divalent substitutional cation and oxygen vacancy defect cluster mentioned, there are several equivalent nearest neighbour positions for those oxygen vacancies. However, when the cluster is deep within the bulk, it does not matter which of these nearest neighbour positions the oxygen vacancy occupies. As the cluster nears the surface, the equivalence of the oxygen vacancy sites with respect to the cation substitutional site at the nearest neighbour becomes broken. In particular, the distance of the oxygen vacancy to the surface is different in different nearest neighbour configurations. It is therefore expected that the energies of the different nearest neighbour configurations will be different, due to the extent of relaxation of the planes of atoms being a function of the distance from the surface. For the $\{(Me_U)'': (V_O)^{\cdot\prime}\}$ cluster, there are four unique nearest neighbour configurations with respect to the (111) surface; see Figure 4.5. A calculation was carried out for each of these configurations and subsequently labelled according the position of the oxygen vacancy. The middle plot in Figure 4.4 shows that configuration "a" has a slightly higher energy than the other three cluster configurations at the Region I - Region II boundary. This can be accounted for by the position of the oxygen vacancy in the "a" configuration being closer to the boundary than the other three.



Figure 4.5: The four unique $\{(Me_U)'':(V_O)^{\cdot\cdot}\}$ cluster configurations with respect to the (111) surface (i.e. surface normal), where the arrow indicates the direction of that surface. The notation of the cluster configurations is maintained throughout the text.

Similarly, the cluster configurations with respect to the (110) surface must be considered. These are shown in Figure 4.6. In this case, there are only three unique configurations of the oxygen vacancy with respect to this surface.



Figure 4.6: The four unique $\{(Me_U)'': (V_O)^{\cdot \cdot}\}$ cluster configurations with respect to the (110) surface, where the blue plane indicates this surface.

The configuration of the $\{(Me_U)'': (V_O)^{"}\}$ cluster is more complicated with respect to the (100) surface. As mentioned in the in Section 4.3, the (100) surface of fluorite is a polar surface and therefore inherently unstable. It was also mentioned that defects must be introduced to this surface in order to neutralize the dipole normal to the surface, and that there are three anion terminations considered; see Figure 4.1. However, instead of considering the cluster in each case, it is possible to rely only on two sets of configurations. Since only half of the anion sites on the surface are filled, the oxygen vacancies associated with the divalent fission product can therefore reside on one of two places: either on a site that is directly under a surface oxygen atom or directly below a void on the surface. Revisiting Figure 4.1, this behaviour is evident, as is the similarity of the termination denoted as AB to the A and B configurations. As mentioned, the AB surface termination can be considered a hybridization of the two surfaces. Therefore, the number of unique cluster configurations required for the three (100) surface terminations can be reduced, see



Figure 4.7: The $\{(Me_U)'':(V_O)^{\cdot\cdot}\}$ cluster configurations with respect to the (100) surface, for the three anion terminations considered (see Figure 4.1), where the blue plane indicates the (100) surface.

Figure 4.7 demonstrates that classifying the anion terminations can be simplified by considering the anions either residing directly next to one another or diagonally across from one another. These two classifications can then be applied to the three terminations considered. The A configuration will always have the anions diagonally across from one another and therefore, only the left hand picture in Figure 4.7 applies. The B configuration will always have termination anions situated in horizontal rows, which applies to the right hand picture of Figure 4.7. The hybrid AB configuration, alternates between having anions next to one another and diagonally across from one another and therefore warrants the use of both pictures in Figure 4.7. Again, the notation for each of these cluster configurations is consistently used throughout this chapter. The segregation of rare-gas atoms through the UO_2 lattice has also been investigated. As mentioned in Chapter 3, the low energy solution site of these atoms is a matter of dispute. Here, both Kr and Xe are assumed to reside in the tri-vacancy site, consistent with results from previous studies on stoichiometric UO_2 [154]. It is worth noting that Kr may equally likely reside in a divacancy site, which would result in a charged defect cluster. However, at this time only neutral defects are supported by the periodic repeat computational code.

There are three possible unique geometric configurations of the inert gas defect cluster with oxygen vacancies in nearest neighbour positions, see Figure 4.8. The configuration denoted (i) is the only configuration considered in this segregation study as it was found have the lowest solution energy in the bulk. The present work calculated solution energies of 1.4eV, 1.9eV and 2.2eV respective to configurations (i), (ii)and (iii) in Figure 4.8, which is in agreement with previous studies [36].



Figure 4.8: The three unique, nearest neigbour configurations of the $\{(V_O)^{\cdots}:(Kr_U/Xe_U)^{\prime\prime\prime\prime}:(V_O)^{\cdots}\}$ cluster, where the defect labelled (i) was found to be of the lowest energy and is used in this work.

As was the case with the divalent fission product defect clusters, the orientation of the inert gas defect cluster with respect to surface must be considered. The lowest energy tri-vacancy configuration ((i) in Figure 4.8) can be oriented in three non-equivalent ways with respect to the (111) surface, see Figure 4.9.



Figure 4.9: The three unique $\{(V_O)^{"}:(Kr_U/Xe_U)^{"''}:(V_O)^{"}\}$ cluster configurations with respect to the (111) surface, which is indicated by the arrow. The notation above is used throughout the text.

A calculation for each of the configurations of defect clusters is performed around each uranium layer in increasing depth from the surface. Therefore, the label of each cluster configuration corresponds to a specific cluster. The reader is therefore referred back to Figures 4.5 through 4.9 while examining the results section.

To this point, only the (111) surface has been considered for rare gas Kr and Xe, due to the computational demand of these calculations. Rather, emphasis was put on determining segregation trends for the less computationally intensive defect types.

4.5 Results and Discussion

4.5.1 The (111) Surface

The energy, E_S , is defined to be the difference in energy between a fission product in the bulk and at the surface. It is therefore possible to compare *relative* energies which elucidate segregation trends. The results of Ce⁴⁺ and Zr⁴⁺segregation to the (111) surface are shown in Figure 4.10. It is clear from this figure that there is a segregation barrier, duly indicated by positive segregation energies: 0.232eV and 0.261eV for Ce⁴⁺ and Zr⁴⁺. Comparison of segregation trends is also facilitated by a second energy, E_T , which is defined as the difference between the energy of the fission product at the surface and the energy of the fission product in its most stable position, often just beneath the surface. In this regard, Zr^{4+} behaves slightly different than Ce^{4+} . For Zr^{4+} , $E_T^{Zr} = 0.352eV$, which is considerably greater than E_S , suggesting that Zr^{4+} will not segregate to the (111) surface, but will remain trapped just below the surface. This trap is not evident for Ce^{4+} , with $E_T^{Ce} - E_S^{Ce} = 0.004eV$. It is likely that the disparity in ionic radii between U^{4+} and Zr^{4+} (0.89 vs. 0.72 Å respectively) gives rise to the subsurface trapping phenomenon, while the similarity in ionic radius between U^{4+} and Ce^{4+} (0.89 vs. 0.87 Å respectively [6]) may explain the lack of trapping.



Figure 4.10: The calculated relative energies of $(Ce_U/Zr_U)^{'''}$ as a function of depth from the (111) surface, where E_T is the trap energy and E_S is the segregation energy.

It should be noted that the manner in which segregation trends are calculated in this work differs from the method of Slater *et al.* [187] as discussed in Section 4.2.2. In their work, Slater *et al.* define E_s as the difference between the energy of a defect in the bulk and at the surface. Srolovitz *et al.*, as previously mentioned in Section 4.2.2, make note of this limitation of the Langmuir - McLean analysis, citing that segregation to subsurface layers is appreciable. The methodology of this work (i.e. performing a calculation at each atomic layer, from the surface to the bulk), describes the segregation behaviour at each atomic layer, rather than only comparing the surface to the bulk. Nevertheless, this is still only part of the complete picture as kinetic barriers to migration of fission products to surfaces are not considered.

In Figure 4.11, it is clear that there is a pronounced driving force for both Ba²⁺ and Sr²⁺ to segregate to the (111) surface of UO₂. The segregation energies for Ba²⁺ and Sr²⁺ are $E_S^{Ba} = -2.706$ eV and $E_S^{Sr} = -1.603$ eV respectively. Clearly, the driving force for Ba²⁺ to segregate is greater than for Sr²⁺. Again, this disparity in E_S can be attributed to ionic radius mismatch. The ionic radius for Sr²⁺ (1.18Å) is more similar to U⁴⁺ (0.89Å) than is the radius for Ba²⁺ (1.35Å).

Figure 4.11 also shows that within the bulk (i.e. >11Å from the surface) there is practically 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).



Figure 4.11: The calculated relative energies of the $\{(Ba_U/Sr_U)'':(V_O)''\}$ defect cluster as a function of depth from the (111) surface, where E_S is the segregation energy.

Simulations involving Xe and Kr proved to be very difficult and only preliminary results were obtained. These are presented in Figure 4.12. The complexity of the Schottky trio made calculations of this type difficult. More calculations are needed in order to make a more reliable and systematic statement. However, the indication from Figure 4.12 is that Kr does not segregate to the (111) surface. It is even more difficult to make a statement about Xe segregation from Figure 4.12. Nevertheless, it appears that for the (a) configuration, there is a segregation barrier. However, calculations for the (b) and (c) configurations have not been completed to the extent that an argument for or against segregation can be made.



Figure 4.12: The calculated relative energies of $\{(V_O)^{"}:(Kr_U/Xe_U)^{"''}:(V_O)^{"}\}$ as a function of depth from the (111) surface.

Another apparent problem with this simulation is that in the bulk, the different cluster configurations do not have the same energy. As previously mentioned, this is because the cluster is approaching the Region I - Region II boundary. Thus, the cluster causes a distortion to the lattice that cannot be propagated into Region II, and therefore, the energy can only be partly minimized. Since the oxygen vacancies associated with the different orientations are at different distances from the Region I - Region II boundary, this causes the different orientations to have different energies.

The position of the fission product relative to the Region I - Region II boundary will also have an effect on the total polarization energy of the lattice. That is, a fission product at the centre of Region I will polarize Region I to a greater extent than if it is at the Region I - Region II boundary. This is again because Region II is not polarizable. This limitation manifests itself in an unphysical effect where as the fission product moves from the boundary into Region I, the polarization energy increases (before the effect of the surface is encountered). Fortunately, such an effect seems negligible in the results on UO_2 presented here (however, it is more apparent in the results on ZrO_2 presented in the Appendix).

4.5.2 The (110) Surface

There are similarities between the two plots in Figure 4.13, the most obvious being that the trends predict the same tendency for Ce⁴⁺ and Zr⁴⁺ to not segregate to the (110) surface, as was the case with the (111) surface. Upon closer inspection, it is clear that the segregation energy barrier for Ce²⁺ is greater than that of Zr⁴⁺, where $E_S^{Ce} = 0.667 \text{eV}$ and $E_S^{Zr} = 0.132 \text{eV}$. These energies should be compared to those obtained for the (111) surface (i.e. 0.232 eV and 0.261 eV for Ce⁴⁺ and Zr⁴⁺ respectively). Thus, the segregation barrier for Ce⁴⁺ is 0.435 eV larger for the (110) than for the (111) surface, while the segregation barrier for Zr⁴⁺ is 0.099 eV smaller. Regardless, both segregation energies are positive, consistent with suggesting no Ce^{4+} or Zr^{4+} segregation to the (110) surface. Also, the energy of Ce^{4+} within the bulk appears to vary more smoothly than Zr^{4+} . This can again be attributed to the similarity in size between Ce^{4+} and U^{4+} , compared to U^{4+} . Consequently, the alternate compression and dilation of atomic layers which characterizes the (110) surface of the fluorite structure [44] has a greater effect on the relative energies of Zr^{4+} than on Ce^{4+} .



Figure 4.13: The calculated relative energies of $(Ce_U/Zr_U)^{'''}$ as a function of depth from the (110) surface.

Figure 4.14 presents the results for Ba^{2+} and Sr^{2+} segregation to the (110) surface. It is clear that both fission products tend to segregate to this surface, as was the case for the (111) surface. Also evident in Figure 4.14 is that E_S^{Ba} is considerably more negative than E_S^{Sr} , suggesting a stronger tendency for Ba^{2+} to segregate than Sr^{2+} . An interesting comparison can be made between the segregation energies of both species to the (110) and (111) surfaces. The energy of segregation, E_S , for both Ba^{2+} and Sr^{2+} to these two surfaces is very similar: $E_S^{Ba} = -2.695eV$ for the (110) and = -2.706eV for the (111); $E_S^{Sr} = -1.604eV$ for the (110) and = -1.603eV for the (111).

Another interesting comparison between Ba^{2+} and Sr^{2+} segregation to the (111) and (110) surfaces is that the fall in energy (and thus the driving force for segregation) begins between 6 and 8Å from the (110) surface, but between 4 and 6Å for the (111) surface. Consequently, it might be expected that a greater amount of Ba^{2+} or Sr^{2+} will be adjacent to the (110) surface than the (111) surface, despite the similarity in segregation energies, E_s .



Figure 4.14: The calculated relative energies of the $\{(Ba_U/Sr_U)'':(V_O)^{"}\}$ defect cluster as a function of depth from the (110) surface, where E_S is the segregation energy.

4.5.3 The (100) Surface

Figure 4.15 depicts the results for Ce^{4+} and Zr^{4+} segregation to each of the three anion terminations described in Section 4.3 for the (100) surface. The top image in Figure 4.15 describes the segregation trends of Ce^{4+} . What is interesting about this plot, is that the segregation energies for each anion termination are different: -0.1221eV, 0.3292eV and 0.098eV for the A, B and AB terminations respectively. Although these are not large energies, it is evident that segregation is a function of the configuration of the anion terminations for polar surfaces. This effect is again evident in the bottom plot in Figure 4.15, describing the segregation trend of Zr^{4+} to the three anion terminations of the (100) surface. Unfortunately, this plot is less compelling as the two energies of the defect near the (100)AB would not successfully minimize. However, what can be seen is that for the (100)A and (100)B surfaces, there is a significant negative segregation energy: -0.7495 and -0.9141 respectively. This suggests that Zr^{4+} will segregate to these two surfaces.



Figure 4.15: The calculated relative energies of the $\{(Ba/Sr_U)'':(V_O)''\}$ defect cluster as a function of depth from the three anion terminations of the (100) surface.

When comparing Figure 4.15 with Figures 4.10 and 4.13, the segregation trends for Ce^{4+} and Zr^{4+} to the three surfaces are clearly different. For both Ce^{4+} and Zr^{4+} , the trend to segregate to the (100)A surface is opposite that calculated for the (111) and (110).

Figure 4.16 shows the results for Ba^{2+} and Sr^{2+} segregation to the (100)A surface. Immediately, when comparing Figure 4.16 with Figures 4.11 and 4.14, clear differences are apparent. Although the segregation energies for Ba^{2+} and Sr^{2+} are again negative ($E_S^{Ba} = -4.8527$ eV and $E_S^{Sr} = -3.2844$ eV), suggesting that these fission products will segregate to this surface, the profile of the energy from the bulk to the surface is different than observed for the previous two surfaces. In both cases, the "c." cluster configuration steadily decreases in energy as it moves to the surface, while the other three configurations decrease in energy more abruptly near the surface. Also in both cases, the "a." configuration is of lower energy throughout the segregation profile than the "b." and "d." configurations. Referring back to Figure 4.7, both the "a." and "c." configurations lie underneath a surface oxygen, while the "b." and "d." configurations lie underneath a surface vacancy. This may contribute to the lower energy. It should also be noted that the segregation energies are substantially more negative than for the previous two surfaces. Again, \mathbf{E}_{S}^{Ba} is more negative than E_S^{Sr} , which can be attributed to size of these ions, as was the case for the previous two surfaces.

Calculations which determine the segregation trends to the (100)B and (100)AB have not yet been successful.



Figure 4.16: The calculated relative energies of the $\{(Ba_U/Sr_U)'':(V_O)''\}$ defect cluster as a function of depth from the (100)A surface, where E_S is the segregation energy.

4.6 Conclusions

The manner in which the segregation energy, E_s , of a given fission product varies between surface types has been demonstrated. Furthermore, E_s has been shown to be a strong function of defect cluster configuration with respect to surface as well as anion termination of the polar (100) surface. These results suggest that release of fission products from grains of UO₂ in nuclear fuel will not be isotropic. Consequently, the distributions of surface types will influence fission product release. This is particularly important when it is considered that surface types will change due to grain growth *in situ* as a function of burn-up. As fission product release is a limiting factor in fuel performance, these results suggest that release may be controlled to an extent through surface modification.

Qualitative comparison can be made to the work of Sato *et al.* [198]. In this work, Sato *et al.* investigated the behaviour of Ba and Zr in fuel specimens irradiated up to burnups of 13.3at% at the experimental fast reactor of the Japanese Nuclear Cycle Development Institute. Although the samples studied were polycrystalline, and the surfaces were not analyzed, it might be deduced that these samples were predominantly consisting of low energy surfaces (i.e. (111) and (100)). Using X-ray micro scanning and X-ray micro analysis to determine radial distributions of Ba and Zr, Sato *et al.* found Ba concentrations to increase in the radial direction, while the Zr concentration remained homogenous in the radial direction. This observation suggested to the authors that Ba easily migrates, while Zr remains in the fuel [198]. If the predominant surface of the fuel is assumed to be the (111) surface, the positive segregation energies calculated for these two species to these two surfaces suggest that the calculations presented in this chapter preliminarily account for this phenomenon, although much more analysis is required.

More calculations are need in order to formulate a systematic statement about

fission product segregation behaviour. At the time these calculations were made, the complexity and size was at the limit of computing resources. As this technology improves, these calculations will become possible. Nevertheless, this chapter clearly shows that the phenomenon of fission product segregation is quite complicated.