Swelling due to the partition of soluble fission products between the grey phase and uranium dioxide

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ABSTRACT

The change in volume associated with the partition of soluble cations from uranium dioxide into the $(Ba,Sr)ZrO_3$ grey phase has been investigated using atomic scale simulations. Here past work on the thermodynamic drive for the segregation of trivalent and tetravalent cations from uranium dioxide is built upon in the context of fuel swelling. Only small tetravalent cations segregate into the grey phase and this is predicted to result in an overall reduction in fuel volume. Individual trivalent cations that segregate, can cause either a contraction or an expansion of the overall fuel volume. Cr_2O_3 doped UO_2 promotes co-partition forming mixed cation clusters in the grey phase and causing an overall reduction in fuel volume for all trivalent cations. This may have implications for fuel performance and may alter other fuel swelling mechanisms.

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1. Introduction

The majority of fuel performance codes rely on empirical data collected over many years of operating experience. Although this has proved to be sufficient, future advances in efficiency and performance will require better understanding of in-reactor materials behaviour. In particular, fuel swelling models could benefit from a deeper mechanistic understanding of the formation of bubbles, precipitates and, in the fuel lattice, accommodation of fission products (FPs) or additives at an atomistic level. In particular, FPs cause the lattice to swell or contract depending upon how they are accommodated. Middleburgh et al. (2012a) used atomic scale modelling to predict the swelling of UO_2 and UO_{2+x} due to the solid solution of fission products. These authors also predicted the energetics associated with the segregation of FPs to $(Ba,Sr)ZrO_3$ (Cooper et al., 2013), the so called grey phase precipitate observed experimentally in irradiated fast breeder reactor (FBR) fuel (Kleykamp et al., 1985), U–Pu mixed oxide fuel above 4% burnup (Sari et al., 1979) and SIMFUEL (Lucuta et al., 1991). Here we extend these studies by predicting the volume changes associated with fission products in the grey phase.

The grey phase consists of elements that are accommodated at two cation sites within the cubic perovskite lattice, the main constituents of which are Ba^{2+} and Zr^{4+}, forming $BaZrO_3$. It is also often termed $(Ba,Sr)ZrO_3$ to reflect the significant Sr^{2+} component that substitutes at the perovskite A site (Kleykamp et al., 1985). More accurately it could be described as $(Cs,Ba,Sr)(U,Mo,Zr)O_3$ although other elements can also substitute into this oxide lattice (Kleykamp et al., 1985; Sari et al., 1979; Lucuta et al., 1991).

The solubility of Sr, Cs and Xe into SrO, BaO and MgO (Liu et al., Sickafus; Liu et al., 2010) has been investigated using density functional theory (DFT) calculations, and into UO_{2+x} (Nerikar et al., 2011) using DFT + U. Similarly, Brillant et al. (2011) also studied the solution of He, Kr, I, Te, Ru, and Ce into UO_{2+x}. Alternatively, in recent work the stability of a wide range of FPs in UO_2 and UO_{2+x} has been assessed with respect to their relative binary oxides using geometry optimised empirical pair potentials (Middleburgh et al., 2012b). This followed from earlier work (Grimes and Catlow, 1991) that considered the possibility that some FPs, especially Ba, Sr, and Zr, could form perovskite ternary oxides rather than binary oxides. This made a considerable difference to the relative solubility of these specific FPs. The earlier study did not, however, consider the possibility that other species might substitute into the perovskite phase or binary oxides as an alternative to remaining in the UO_2 or UO_{2+x} lattice (as has been observed experimentally (Kleykamp et al., 1985; Sari et al., 1979)). Cooper et al. (2013) used the static empirical pair potential approach to consider the relative solubility of an extensive range of trivalent and tetravalent cations into $BaZrO_3$ and $SrZrO_3$ (as end members of $(Ba,Sr)ZrO_3$), from their equilibrium sites in UO_2 and UO_{2+x} (as recently identified (Middleburgh et al., 2012b)). Isovalent segregation at Zr^{4+} sites was predicted for the tetravalent cations Ru^{4+} and Mo^{4+}. Furthermore, a

number of trivalent cations were found to segregate into $BaZrO_3$ and $SrZrO_3$ from stoichiometric UO_2 forming either $\{2T'_{Zr} : v^{\bullet\bullet}_O\}^\times$ or $\{T^\bullet_A : T'_{Zr}\}^\times$ defect clusters depending on cation size (where A represents either Ba^{2+} or Sr^{2+}, T indicates a trivalent cation and v represents a vacancy defect using Kroger–Vink notation (Kröger and Vink, 1956)). Firstly, we examine the change in lattice volume (defect volume) of $BaZrO_3$ and $SrZrO_3$ associated with the accommodation of such defect clusters. Secondly, by combining these results with the defect volumes in UO_2 (calculated by Middleburgh et al. (2012a)) it is possible to examine the combined changes in lattice volume of both phases due to the partition of fission products between UO_2 or UO_{2+x} and the grey phase.

2. Methodology

Atomic scale geometry optimisation simulations were carried out using the classical Born ionic lattice approximation within the GULP code (Gale, 1997) and do not, therefore, account for kinetic behaviour such as diffusion or radiation damage. The classical empirical pair potential description of inter-ionic interactions involves two parts; short-range interactions modelled using the parameterised Buckingham potential (Buckingham, 1938) and long-range Coulombic interactions. Together these describe the energy of interaction between two ions, i and j, as:

$$E_{ij} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + A_{ij}\exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \tag{1}$$

The ionic charges, q_i and q_j, that determine the Coulombic energy assume formal charge values (e.g. O^{2-}). The second and third terms together form the Buckingham potential. A_{ij} and ρ_{ij} parameters in the Buckingham potential describe the repulsive short-range interactions between each ion; the C_{ij} term describes the attractive van der Waals interaction (Hamaker, 1937). The polarisability of the oxygen ion is included by considering it as a positive charged ionic core attached to a negative charged shell where energy is harmonic with respect to the core–shell displacement (Dick and Overhauser, 1958). The parameters used in this study have been reported previously for the O^{2-}–O^{2-} (Binks and Grimes, 1994), U^{4+}–O^{2-} (Middleburgh et al., 2012b) and for divalent, trivalent and tetravalent cation–oxygen interactions (Levy et al., 2007; Grimes and Pilling, 1994; Busker et al., 1999; Zacate et al., 2000).

Defect energies of clusters in the dilute limit are calculated using the Mott-Littleton approach (Mott and Littleton, 1938) where the region I and region IIa radii are 13.0 Å and 34.0 Å respectively (Cooper et al., 2013; Middleburgh et al., 2012b). The radii chosen ensure the zirconium vacancy, v''''_{Zr}, defect energy is converged to within 0.1 eV for both the $BaZrO_3$ and $SrZrO_3$ phases. The volume change of a crystal due to defect formation can be determined by examining the defect energy as a function of lattice parameter for a number of external pressures using the following relationship:

$$V = -\frac{c_0 k_T}{3}\frac{df}{dc} \tag{2}$$

where k_T is the isothermal compressibility, c_0 is the lattice parameter at zero pressure and df/dc is the first derivative of the defect energy, f, as a function lattice parameter, c. The defect energy, f, is calculated at a number of pressures from -1 GPa to 1 GPa and plotted against the perfect crystal lattice parameter, c, for a given pressure. Typically the relationship is linear and the gradient gives df/dc. The changes in lattice volume of the $BaZrO_3$ and $SrZrO_3$ crystals due to fission product accommodation are combined with the defect volumes in the UO_2 phase (calculated by Middleburgh
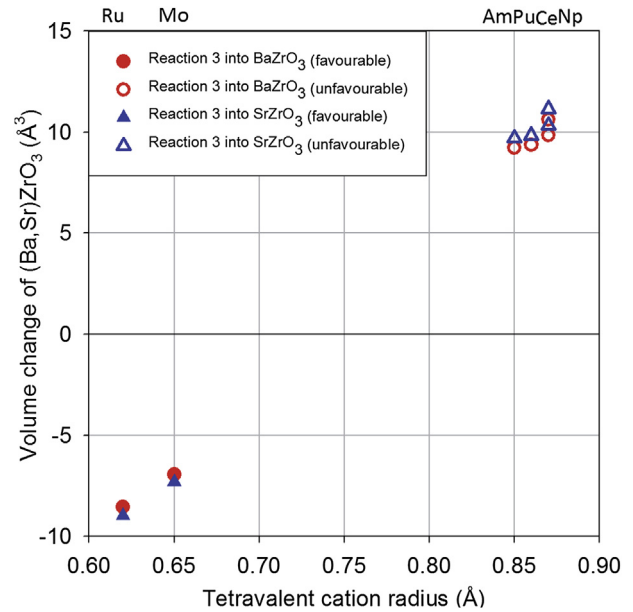

Fig. 1. Change of lattice volume associated with the substitutional defects, $M^\times_{Zr}$, formed by the accommodation of tetravalent cations in $BaZrO_3$ and $SrZrO_3$, as a function of ionic radius (Shannon, 1976), by isovalent substitution at Zr^{4+} sites (reaction 3). Filled symbols identify reactions that are energetically favourable, unfavourable reactions are shown by open symbols (Cooper et al., 2013).

et al. (2012a)) to give net volume changes of both phases due the most favourable partition reactions (as identified previously (Cooper et al., 2013)).

3. Results and discussion

3.1. Swelling due to tetravalent cation partition into $(Ba,Sr)ZrO_3$

The lowest energy partition mechanism for tetravalent cations (M) from both UO_2 and UO_{2+x} (for tetravalent cations they are identical) into $BaZrO_3$ or $SrZrO_3$ has been previously identified as isovalent accommodation at Zr^{4+} sites via reaction 3 (Cooper et al., 2013).

$$\overline{M^\times_U} + Zr^\times_{Zr} \rightarrow \overline{Zr^\times_U} + M^\times_{Zr} \tag{3}$$

The lattice volume changes due to the substituted defects in $BaZrO_3$ and $SrZrO_3$ (i.e. $MM^\times_{Zr}$) are shown in Fig. 1. Tetravalent cations that have negative partition energies are predicted to segregate to the grey phase (Cooper et al., 2013) (represented by filled symbols) and all form defects that result in a contraction of $BaZrO_3$ and $SrZrO_3$. Conversely, those that have positive partition energies (represented by open symbols) were all predicted to cause an expansion of $BaZrO_3$ and $SrZrO_3$. However, as they are not predicted to segregate to the grey phase only tetravalent cations with negative volumes will be observed.

The combined volume change of both phases due to reaction 3 is the difference in defect volumes for the cations in UO_2 or UO_{2+x} (Middleburgh et al., 2012a) and in the grey phase. It predicts the net volume change due to tetravalent cation partition into $(Ba,Sr)ZrO_3$ (see Fig. 2). Small tetravalent cations, such as Ru^{4+} and Mo^{4+}, do segregate to $(Ba,Sr)ZrO_3$, and as a result there is an overall contraction. Conversely, tetravalent cations with ionic radii greater than that of Zr^{4+} will expand the fuel through reaction 3 but, as previously stated, partition is energetically unfavourable for these large tetravalent cations (Cooper et al., 2013). Thus, segregation of