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The diffusion of iodine and caesium in the $UO_{2\pm x}$ lattice

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Abstract

The migration activation enthalpies of caesium and iodine in $UO_{2\pm x}$ predicted using atomistic simulation methodology, depend greatly on fuel stoichiometry. The mechanisms for stoichiometric and non-stoichiometric fuel require uranium self-diffusion, with the exception of iodine in UO_{2-x} which employs an anion vacancy mechanism. The iodine post-irradiation results compare very well with the predicted activation enthalpy. In-pile iodine release experiments suggest a reduced activation enthalpy for iodine migration. The diffusion model presented allows for this result if uranium diffusion were greatly affected by the irradiation conditions. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The solution and migration behaviour of fission product ions in uranium oxide fuel are important parameters for safety studies, since the first stage in any mechanistic model of fission product release (e.g., [1]) is that of migration of the fission product to the grain boundaries The release of fission products from the lattice depends on temperature, the solution enthalpy of the fission product ion and its migration enthalpy. Both the solution and migration enthalpies can vary greatly with fuel stoichiometry

The solubilities of Cs and I in UO_2 are known to be very low [2,3]. Theoretical simulations predict high (i.e. unfavourable) solution enthalpies for stoichiometric UO_2 which are significantly reduced for hyper-stoichiometric UO_{2+x} [4].

Many studies have been devoted to the release of fission products from UO_2. Prussin et al. [5] have studied the post-irradiation release of Cs, I and other fission products from poly-crystalline UO_2 with a grain size of approximately 10 μm. Similar release experiments, but at lower temperatures, were performed by Akabori and Fukuda [6]. The data from Prussin et al. were treated using the Booth [7] model as described in Akabori and Fukuda [6] and plotted in Fig. 1. The Arrhenius equations for the fits in Fig. 1 are listed in Table 1.

Results for iodine from Prussin et al. contain some scatter but seem to suggest an activation enthalpy of 5.8±2.0 eV. Studies by Friskney and Turnbull [8] on iodine release during irradiation show an activation enthalpy of 2–3 eV above 1300 K. The results of these two studies are compared in Fig. 2. At temperatures below 1200–1300 K, as discussed by Friskney et al. [9] release does not occur via purely thermal processes but is highly influenced by recoil and knock-out contributions. Therefore it is not appropriate to compare the results presented in this study with experimental data derived at such low temperatures.

The Arrhenius energies predicted by Friskney and Turnbull are much lower than those suggested by Prussin et al. This is not surprising as the Friskney and Turnbull results were obtained from in-pile experiments, where radiation damage rather than thermal processes may be responsible for the formation of intrinsic defects which assist the diffusion of fission products [10].

Here we will use atomistic scale simulation to predict activation energies for fission product migration within the uranium lattice. These results will then be discussed in the light of the experimental data summarised above.

2. Methodology

Mott–Littleton methodology [11] is used to calculate solution and migration enthalpies. This technique is

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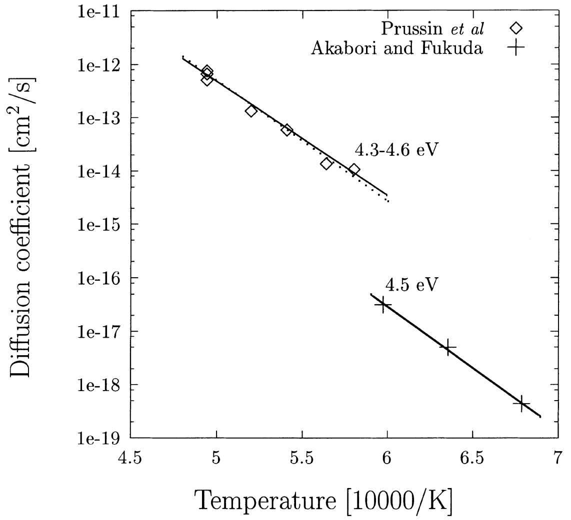

Fig. 1. An Arrhenius plot of caesium release data taken from Prussin et al. [5] and Akabori and Fukuda [6]. The activation enthalpies of the fits are indicated in the figure. Details of the fits are given in Table 1.

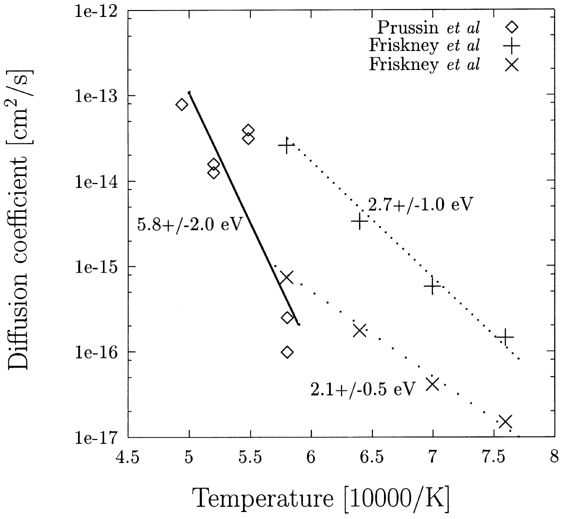

Fig. 2. An Arrhenius plot of the diffusion coefficients of iodine in UO_2 according to Friskney et al. [8] and Prussin et al. [5] with some suggested activation energies. Details of the fits are listed in Table 1.

based on the Born ionic description of forces between ions in the lattice. Defects are embedded in a spherical region of the lattice surrounding the defect. In this first region, the lattice and defect ions interact via the Coulomb force and via parameterised short-range interactions, that is, forces are modelled explicitly. Beyond this spherical region the Mott–Littleton approximation is used to calculate the interaction of the lattice with ions in the defect region. The most stable positions of ions in the inner region are then found using energy minimisation. The parameters for the short range interactions were derived by Grimes and Catlow [4]. The methodology is described in greater detail in [4,11]

The prediction of the solution enthalpy of an ion is made by evaluating the solution reaction, for instance

$$Cs_2O + 2U_U^{\times} + 3O_O^{\times} \overset{UO_2}{\rightarrow} 2Cs_U^{\prime\prime\prime} + 3V_O^{\cdot\cdot} + 2UO_2, \qquad (1)$$

where each component defect energy is calculated separately. This particular reaction is for Cs_2O solution in UO_{2-x}. The enthalpy for solution in UO_2 and UO_{2+x} can be obtained by considering the availability of Frenkel defects in the material and adjusting the solution reaction accordingly. Using reaction 1, for example, the solution enthalpy for Cs_2O in UO_{2+x} can be evaluated by removing $3V_O^{\cdot\cdot}$ from the right and adding $3O_i^{\prime\prime}$ to the left side of the reaction, reflecting the larger concentration of $O_i^{\prime\prime}$ ions in UO_{2+x}. More details are given in [4].

For ions which may exhibit different charge states, the most likely state can be predicted by considering the ionisation energy and the electron affinity of the host lattice [4].

To predict which mechanism will be responsible for fission product migration it is first necessary to determine the lowest energy solution site. (These were reported for each case previously [4].) It is then possible to decide if transport will occur via an interstitial or a vacancy assisted migration mechanism. However, interstitial sites were never preferred energetically over substitutional sites. In addition, in no experimental

Table 1
Fitted Arrhenius equations for Cs and I release data taken from Refs. [5,6,8]

Caesium		
1473–1673 K	$D(T) = 1.5 \times 10^{-3} \exp(-4.5\ \mathrm{eV}/kT)$ (cm^2/s)	Ref. [6]
1723–2023 K (Fit includes all points)	$D(T) = 3.4 \times 10^{-2} \exp(-4.3\ \mathrm{eV}/kT)$ (cm^2/s)	Ref. [5]
1723–2023 K (Fit ignores lowest temperature point)	$D(T) = 2.6 \times 10^{-1} \exp(-4.6\ \mathrm{eV}/kT)$ (cm^2/s)	Ref. [5]
Iodine		
1200–1700 K (small grain 20–40 μm)	$D(T) = 1.2 \times 10^{-9} \exp(-2.1\ \mathrm{eV}/kT)$ (cm^2/s)	Ref. [8]
1200–1700 K (large grain ∼150 μm)	$D(T) = 2.4 \times 10^{-6} \exp(-2.7\ \mathrm{eV}/kT)$ (cm^2/s)	Ref. [8]
1723–2023 K (small grain ∼10 μm)	$D(T) = 4.3 \exp(-5.4\ \mathrm{eV}/kT)$ (cm^2/s)	Ref. [5]

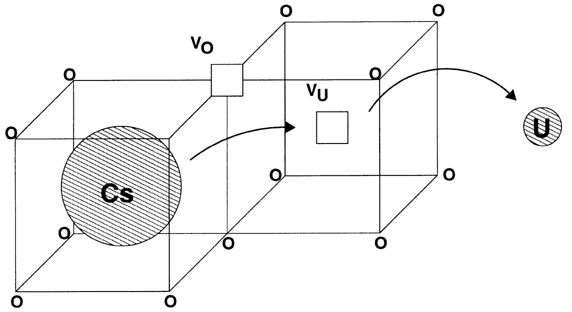

Fig. 3. The cation vacancy assisted migration mechanism by which Cs migrates in UO_{2+x}. This mechanism is also responsible for iodine migration in UO_{2+x}.

studies were interstitial mechanisms considered. Interstitial controlled mechanisms are therefore not discussed further.

Given a vacancy assisted mechanism, it is necessary to determine:

- The formation enthalpy of the solution (trap) site or sites involved.
- The migration enthalpy from one trap site to the next.
- If the process is controlled by self-diffusion of intrinsic defects.

The formation enthalpies of the solution sites involved can be calculated by constructing solution reactions such as Eq. (1) and simulating all the defects therein. From that solution site an ion can migrate by attracting one or more vacancies and moving internally within this defect aggregate. Finally a vacancy is emitted upon which the fission product returns to the original state but translated by one lattice position. An example of such a mechanism is shown schematically in Fig. 3 for migration via uranium vacancies with support from one or more oxygen vacancies. The internal migration enthalpies in such processes are determined by placing the ion at consecutive positions along the migration path and relaxing the lattice surrounding the fission product at each step. From this an energy profile of the migration process is constructed.

If the migration process relies on intrinsic self-diffusion process and if this has a higher activation enthalpy than the migration process itself, then the observed fission product migration enthalpy will be that of the self-diffusion process. The activation enthalpy for self-diffusion of uranium has been taken from the experimental results of Matkze [12] and is 5–7.8, 5.6 and 2.6 eV for UO_{2-x}, UO_2 and UO_{2+x}, respectively.

3. Results

Table 2 summarises the present results for Cs and I ions in UO_{2-x}, UO_2 and UO_{2+x}. For each ion and stoichiometry range the solution enthalpy, solution site, proposed migration mechanism and migration enthalpy are reported. Additionally, for iodine the predicted charge state is given.

Reiterating the conclusions of Grimes and Catlow [4]:

- Caesium is predicted to be insoluble in UO_{2-x} and UO_2, but becomes soluble in UO_{2+x} as the uranium vacancies necessary to accommodate caesium are more easily formed in UO_{2+x}.
- Iodine is associated with oxygen vacancies in UO_{2-x}, with uranium and oxygen vacancy complexes in UO_2 and with uranium vacancies in UO_{2+x}.
- The solution enthalpies are clearly reduced when UO_2 is oxidised from the stoichiometric composition.
- For iodine, predicted solution enthalpies are evaluated relative to free iodine gas. If compounds

Table 2
Predicted solution enthalpies and migration activation enthalpies of Cs and I in UO_2 as a function of stoichiometry

	UO_{2-x}	UO_2	UO_{2+x}
Caesium			
ΔH_S	4.96 eV	4.47 eV	−0.61 eV
Trap	$Cs^{\cdot}_{UO_2}$	Cs'''_U	Cs'''_U
Migration mechanism	Via $Cs^{\cdot}_{U_2O_4}$	Via $Cs'''_{U_2O_2}$	Via Cs'''''_{U_2O}
Process ΔH_M	5.9 eV	4.7 eV	3.4 eV
Rate determining step	Depends on x	U self-diffusion	Migration process
Predicted ΔH_M	5.9–7.8 eV	5.6 eV	3.4 eV
Iodine			
ΔH_S	7.99 eV	10.66 eV	0.17 / 2.71 eV
Charge state	I^-	I^-	I^{2+} / I^+
Trap	$\{ I^{\cdot}_O : V^{\cdot\cdot}_O \}^{\cdot\cdot\cdot}$	$\{ I^{\cdot}_O : V''''_U \}'''$	I''_U / I'''_U
Migration mechanism	Via $I^{\cdot}_O$	Via I_O and I_{UO_2}	Via I_{U_2O}
Process ΔH_M	1.0 eV	1.7 eV	5.1 eV / 6.3 eV
Rate determining step	$I^{\cdot}_O$ formation	U self-diffusion	Internal migration
Predicted ΔH_M	1.0 eV	5.6 eV	5.1 eV / 6.3 eV

containing iodine form outside the fuel matrix then, it is clear that the solution energy will only become less favourable. In the cases of solution in UO_{2-x} and UO_2 such an effect is of no practical significance since the solution enthalpies are already so high (i.e. zero solution). However, in UO_{2+x}, where the solution enthalpy is rather small a modest increase could reduce the solubility of iodine significantly.

An isolated atom in a host lattice is a unique chemical environment where the notional charge states adopted by the atom are governed by energy minimisation within the lattice as a whole. To this end, the possibility of the 'unusual' I^{2+} charge state has been considered alongside the more common $I^-/I^0/I^+$. Interestingly, the simulations predict that iodine prefers the I^{2+} charge state in UO_{2+x}. However, due to the residual uncertainty as to whether oxidation beyond I^+ is achieved in practice, the results for both I^+ and I^{2+} charge states are discussed.

Caesium migration in UO_{2-x} occurs via the association of one additional uranium vacancy and possibly one or two oxygen vacancies to the Cs_{UO_2} equilibrium trap site. The subscript UO_2 implies that the trap is composed of one uranium and two oxygen vacancies. An internal migration step and the loss of the uranium vacancy complete the migration. The three steps of this mechanism are shown schematically in Fig. 3. The formation of the large trap requires between 4.8 and 5.8 eV, depending on the coordination of the oxygen vacancies. The internal migration step has an activation energy of 1.1 eV and the most likely migration process is therefore predicted to have an overall migration activation enthalpy of 5.9 eV. However, the activation enthalpy for the self-diffusion of uranium vacancies in UO_{2-x} is 5–7.8 eV, depending on the stoichiometry, implying that this is probably the rate determining step.

In stoichiometric UO_2 a similar process is responsible for caesium migration although in this case the caesium ion equilibrium trap site is a single uranium vacancy. The association of a uranium vacancy and two oxygen vacancies results in a $Cs_{U_2O_2}$ cluster which has a relative formation enthalpy of 4.0 eV and an internal caesium migration enthalpy of 0.7 eV. The predicted total energy is therefore 4.7 eV, which is lower than the migration enthalpy of uranium vacancies (5.6 eV) on which this mechanism should then depend.

In UO_{2+x} migration depends more markedly on the internal migration step. Even though the formation enthalpy of a caesium ion trapped in a uranium di-vacancy is lower than that of a tri-vacancy (which has an added oxygen vacancy), the latter is responsible for caesium diffusion as the internal migration enthalpy is greatly reduced by the additional oxygen vacancy. The total migration process requires 3.4 eV (which is higher than the enthalpy for uranium self-diffusion in UO_{2+x}: 2.6 eV).

Iodine migration is different from caesium migration as the ion can exhibit a negative formal charge state in which it traps more easily at oxygen vacancies. In UO_{2-x} it is trapped in an oxygen di-vacancy in which it can be in two positions which are separated by a migration barrier of only 0.3 eV. The loss of a vacancy to form an $I_O^{\cdot}$ is a process which requires 1 eV. As the internal migration step occurs at equilibrium, this is not added to the total process energy and the migration enthalpy is therefore predicted to be 1 eV (i.e. higher than the energy for oxygen self-diffusion).

The reduced availability of oxygen vacancies in stoichiometric UO_2 forces the I ion (still with a charge state of -1) to occupy a UO di-vacancy, I_{UO}. The dissociation and association of uranium and oxygen vacancies are responsible for the migration although, unlike Cs, I does not need a V_{U_2} cluster to migrate as it can occupy a single oxygen vacancy. Dissociation of the uranium vacancy from the oxygen vacancy trap requires 1.7 eV. The uranium self-diffusion (5.6 eV) therefore controls the process. Despite the much larger process energy due to the necessity for uranium self-diffusion the alternative, where iodine migrates via oxygen vacancies, has an even higher energy.

Assuming that iodine ionizes to I^{2+} in UO_{2+x}, the formation of a di-uranium vacancy from the I_U trap requires 1.6 eV. The internal migration step expends a further 3.5 eV and the predicted migration enthalpy would be 5.1 eV.

If we assume that iodine only ionises to I^+ in UO_{2+x} then the mechanism is the same, but the formation of the di-vacancy requires 2.8 eV and the process totals 6.3 eV.

In the Arrhenius diffusion equation,

$$D(T) = d^2 v \exp\left(\frac{-E_M}{k_B T}\right), \qquad (2)$$

the value we attempt to predict via atomistic simulation is E_M. The assumption here is that diffusion is via the motion of ionic species which means that appropriate estimates for the length of the jump step, d and the attempt frequency v can be made. The jumpstep in UO_2 is $\approx 2.5–4$ Å and the attempt frequency is usually given as $10^{11}–10^{14}$. $D_0 \approx d^2 v$ can therefore be estimated to be $10^{-5}–10^{-1}$ (cm²/s) for UO_2. If we compare the values for D_0 in Table 1 then it is clear that the Arrhenius equations for Cs correspond well with the suggested interval for D_0. However, the D_0 values fitted to iodine experiments show 15 orders of magnitude variation. The results of Prussin et al., show a rather high D_0 whereas those of Friskney suggest a rather low D_0, both slightly outside of the range we would expect from a theoretical point of view.

Fig. 4 shows the Arrhenius equation for 5.6 eV plotted over the available data. The assumed D_0 value is 10 cm²/s which is higher than expected from a theoretical point of view.

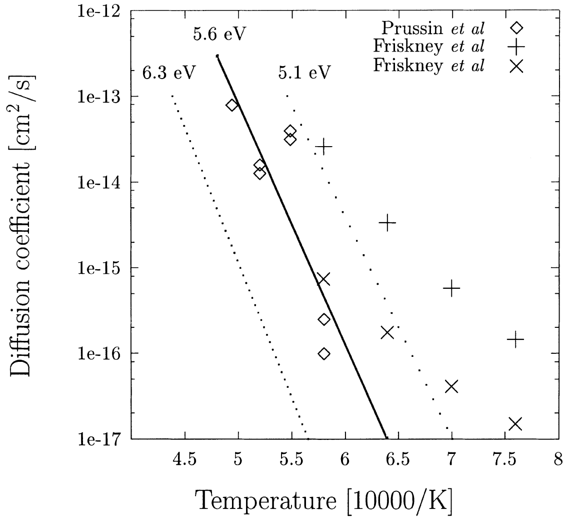

Fig. 4. Comparison of the suggested migration activation enthalpies for iodine with literature data [5,8]. The three lines correspond with the possible predictions for the Arrhenius enthalpy for UO_2 and UO_{2+x}. This figure shows that a value of 5.6 eV is a good prediction for the high temperature ex-pile diffusion in UO_2.

4. Concluding comments

Caesium and iodine are practically insoluble in UO_2 and UO_{2-x}. Furthermore, although both ions show an important reduction of the solution enthalpy in UO_{2+x}, only Cs seems to actually become soluble upon oxidation of the UO_2 lattice.

The experimental activation enthalpy for Cs migration in UO_2 (4.3 eV) is lower than the uranium activation enthalpy for self-diffusion (5.6 eV), which is predicted to be the controlling step in the migration mechanism. If the process were not to depend on the uranium migration, which is possible if, for example, uranium diffusivity were greatly enhanced by radiation damage, then the predicted migration enthalpy would be 4.7 eV. The experimental data summarised in Fig. 1 are certainly consistent with this hypothesis and both sets of experimental data were derived from highly irradiated materials.

The comparison of the predicted iodine activation enthalpy with the experimental data in Fig. 4 shows very good agreement with the trace irradiated post-irradiation results of Prussin et al. [5]. Under irradiation conditions with moderate burnup the migration process seems to proceed via a different mechanism, as the Friskney and Turnbull [8] results show.

One implication of these differences is that irradiation damage can simultaneously affect the diffusion mechanism. The current model allows for this result as it is the uranium self-diffusion that is affected by the irradiation conditions. Clearly further investigation is required since it is the in-pile results of Friskney and Turnbull which would appear most relevant for reactor safety studies.

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