Effect of additives on self-diffusion and creep of UO_2

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Abstract

The creep of UO_2 doped with Nb_2O_5 and Cr_2O_3 has been assessed using a point defect model based on the law of mass action, and the diffusional creep according to the Nabarro-Herring mechanism, which relates the creep rate to the lattice self-diffusivity, the inverse of grain area and the applied stress. The self-diffusion coefficients of cation (U) and anion (O) are directly proportional to the concentrations of ions, which in turn are functions of dopant concentrations. The model has been used to evaluate past creep experiments on UO_2 doped with Nb_2O_5 and Cr_2O_3 in concentrations up to about 1 mol.%, with a varying grain size at different temperatures and applied stresses. The creep rate increases significantly with the dopant concentration and the putative model, after a modification of the creep rate coefficient, retrodict the measured data satisfactorily. A number of factors affecting creep rate and thereby our model computations are discussed.

1. Introduction

Uranium dioxide (UO_2) is the standard nuclear fuel used in commercial light water reactors (LWRs). A LWR core contains fuel assemblies of long (≈ 4 m) cylindrical fuel elements or rods, where each element consists of a zirconium alloy cladding tube containing the UO_2 fuel pellets [1, 2].

Doping the UO_2 fuel with a small amount of certain metal oxides, such as Nb_2O_5 or Cr_2O_3 , will enhance self-diffusion processes considerably at sufficiently high temperatures during reactor service and under sintering in fabrication [3]. This effect leads, inter alia, to a higher fuel creep rate, or more viscoplastic behavior, during reactor operation, thereby causing a softer fuel

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pellet contact with the cladding upon pellet-cladding interaction (PCI). During an increase in reactor power, thermal expansion of fuel can impart large tensile stresses in the cladding upon pellet-cladding contact. Therefore, in the presence of corrosive fission products, stress corrosion cracking of cladding may occur [4, 5]. Since pellet-cladding interaction remains a major technical issue in reactor fuel performance, there is a great incentive to alleviate its severity, e.g. by means of fuel doping; see e.g. [6, 7, 8] and Nonon et al. in [5]. Additives such as Nb_2O_5 or Cr_2O_3 also affect other UO_2 fuel properties, among them fission product gas behavior [9].

Creep behavior of UO_2 fuel is rather complicated. It depends on the oxygen-to-metal ratio, microstructural characteristics, e.g., grain size and shape, porosity, the state variables such as temperature and the stress level, and irradiation condition. Various mechanisms have been suggested to govern UO_2 creep at high temperatures ($\approx 1400\text{--}2300\text{ K}$). These have been reviewed in the literature; see e.g. [10, 11] and the recent paper by Goyal et al. [12]. In brief, one may classify the creep mechanisms into lattice diffusion controlled (Nabarro-Herring), grain boundary diffusion (Coble) and dislocation induced creep. Nabarro-Herring creep accounts for vacancy transport within the grain, with the rate governed by the diffusion of uranium vacancies; while Coble creep describes the diffusion within the grain boundary. The strain rate in both these mechanisms varies linearly with the applied stress [13]. Lifshitz [14] has provided a unified theory of diffusion-viscous flow of polycrystalline solids, which encompasses the Nabarro-Herring-Coble description as well as grain boundary sliding. Dislocation induced creep is due to dislocation climb and glide with the latter being rate controlling under a constant dislocation density [11]. The dislocation density is controlled by the Peierls stress of the crystal [15]. At low stresses, the strain rate varies linearly with the applied stress (Harper-Dorn creep), whereas at higher stresses, a power law dependence on applied stress has been observed [16]. In the literature, as has been stated in [12], there is no concord in regard to the dominant mechanism of thermal creep in UO_2 . Doping UO_2 brings about additional complications to its creep behavior, depending on the type and concentration of the dopant. In this paper, we have chosen the Nabarro-Herring description to analyze experimental data on creep of UO_2 doped with Nb_2O_5 and Cr_2O_3 , obtained in certain ranges of dopant concentration, temperature and applied stress.

The relationship between the self-diffusion and creep in UO_2 is well discussed in the literature, e.g. [13, 17, 18, 19]. In particular, it is known that

there is a strong dependence of uranium self-diffusion and creep rate on the oxygen chemical potential in uranium oxide. That is, a slight increase in oxygen concentration beyond stoichiometry leads to a large increase in diffusivity and creep rate [13, 20, 21]. The creep of UO_2 doped with Nb_2O_5 up to 1.0 mol% in the stress range 0.5-90 MPa at temperatures between 1422 and 1573 K has been studied by Sawbridge et al. [22]. These workers observed that Nb_2O_5 doping can cause a significant increase in the steady-state creep rate so long as niobium ion is maintained in the Nb^{5+} valence state. The effect of oxygen chemical potential on the creep rate of Nb_2O_5 -doped UO_2 was investigated by Ainscough et al. [23], who observed that the creep rate under both tensile and compressive loading was extremely sensitive to the chemical potential of oxygen, i.e. a slight increase in the latter quantity raised the creep rate by two orders of magnitude. Ainscough and coworkers associated this effect with the formation of Nb^{4+} ion [23].

The creep of UO_2 doped with Cr_2O_3 up to 0.35 mol% in the stress range of 20-70 MPa at temperatures ranging from 1573 to 1773 K has been investigated by Dugay et al. [24, 25]. As in the case of Nb_2O_5 , they found a marked increase in creep rate as a function of dopant concentration. Similarly, creep tests performed by Nonon et al. indicate an order of magnitude increase in creep rate for ≈ 0.35 mol% Cr_2O_3 -doped UO_2 relative to that of "pure" UO_2 at 1773 K under a compressive stress of 45 MPa (see page 306 in [5]). Both Nb_2O_5 and Cr_2O_3 are grain growth promoters during UO_2 sintering in fabrication.

The stable phase of uranium dioxide or UO_2 has a fluorite structure for all temperatures up to the melting point. Crystalline UO_2 contains predominantly the ions U^{4+} and O^{2-} . The oxygen ions are arranged on a simple cubic lattice, while the uranium ions form a face-centered cubic (fcc) sublattice. The fluorite structure contains four UO_2 molecules. Uranium dioxide has an intricate electronic structure, namely, it is a Mott-Hubbard insulator [26, 27, 28], which has an antiferromagnetic ordering below 31 K [29, 30, 31] with multipolar interactions between the f-electrons [32].

As-fabricated, i.e. unirradiated, UO_2 fuel contains the usual point defects such as cation and anion vacancies and interstitials. In addition to these, the combination of such point defects is also of prevalent, especially when UO_2 is irradiated. These defects comprise the Frenkel pairs, each made up of a vacancy and an interstitial of the same atom, and Schottky defects, each consisting of two oxygen vacancies and one uranium vacancy, which may be bound or separated [33].

Self-diffusion in oxides with fluorite structures and in particular UO_2 is controlled by the concentrations of point defects, which regulate the oxygen to metal ratio in the material, i.e. the O/U ratio in UO_2 . Additives such as Nb_2O_5 and Cr_2O_3 affect the O/U ratio and thereby change the concentration of point defects. Point defects and self-diffusion in some actinide oxides including UO_2 have been a subject of several past [34, 35, 36] and recent reviews [37, 38]. To date, however, it appears that no new experiments on uranium self-diffusion have been reported in the literature, in contrast to the case for oxygen diffusion.

In this paper, we first consider a point defect model, based on the law of mass action, to relate the concentrations of point defects to that of dopants (Nb_2O_5 or Cr_2O_3) in UO_2 . Then the model is used to express the lattice diffusion coefficients of the point defects as a function of dopant concentration; which in turn is used to calculate the creep strain rate as a function of dopant concentration. We posit that the self-diffusion of U in the extrinsic region is via U^{4+} vacancies for Nb_2O_5 -dopant and via U^{4+} interstitials for Cr_2O_3 -dopant. We assume that the lattice Nabarro-Herring diffusional creep mechanism [39] is prevalent over the temperature and stress region of interest for the systems under consideration.

We begin in Sec. 2 by setting up the point defect equations, expressing the concentrations of anion (oxygen) and cation (uranium) vacancies and interstitials in terms of dopant concentration. Furthermore, the lattice diffusivities for the defects are formulated in this section and their dependence on temperature, assessed from the literature, are collected there. In Sec. 3, we introduce the diffusional creep model, which we will use to compute or retrodict experimental data on creep rate of Nb_2O_5 - and Cr_2O_3 -doped UO_2 . Section 4 will discuss a number of factors affecting our computations. These comprise important input parameters to the model, the mechanisms overriding the diffusional creep processes and the idealization of the putative integral model. This section will also discuss the missing ingredients in our model computations. Finally, we conclude the paper by a summary of the main results and suggestions for further studies and possible model improvements.

2. Point-defect model

In this section, we summarize the various thermodynamic formulas and fix our notation, which will be the basic ingredients of our model. The formulas relate point-defect concentrations to temperature and free energies

of formation of the defects plus the doping content. The considered point-defect model was originally developed by Lidiard [40] for calculation of self-diffusion of uranium in $\text{UO}_{2\pm x}$. The model is based on the premise that the defects accountable for the deviation from stoichiometry are isolated non-interacting point defects. Here, we adapt this model to the case of metal-oxide additives of type M_2O_5 (pentavalent) and M_2O_3 (trivalent), where M stands for metal, in UO_2 .

2.1. Law of mass action

Crystalline solids, in particular ionic solids, embrace a whole range of interacting defects, where reactions between them finally lead to equilibrium. Typical reactions may be expressed in general in the form

$$\sum_{i=1}^N n_i X_i \rightleftharpoons \sum_{i=1}^N \nu_i Y_i, \quad (1)$$

where n_i , ν_i are the number of species X_i , Y_i in the reactant and product components. Now the law of mass action states that, in equilibrium, the concentrations $[X_i]$, $[Y_i]$ satisfy the relation [41, 42]

$$\frac{\prod_{i=1}^N [X_i]^{n_i}}{\prod_{i=1}^N [Y_i]^{\nu_i}} = K(T), \quad (2)$$

where the reaction parameter K depends on temperature and pressure, but not on the concentrations; it is also called the chemical equilibrium constant [41]. Generally, K has an Arrhenius form $K(T) \propto \exp(-\Delta E/k_B T)$, where ΔE is the free energy absorbed in the forward reaction and k_B is the Boltzmann constant [42, 43].

We want to apply the law of mass action (2) to the concentrations of the Frenkel and Schottky defects in doped UO_2 . The chemical reactions for the formation of defects in UO_2 are

Here, subscripts v and i represent vacancy and interstitial, respectively.

Thus, applying (2) to reactions in (3), with $[\emptyset] = 1$, gives

$$[\text{O}_v][\text{O}_i] = K_1, \quad (4a)$$

$$[\text{U}_v][\text{U}_i] = K_2, \quad (4b)$$

$$[\text{O}_v]^2[\text{U}_v] = K_3. \quad (4c)$$

Besides (4), the conservations of the mass and charge need to be satisfied. The former is written as

$$2[\text{U}_v] + [\text{O}_i] = 2[\text{U}_i] + [\text{O}_v] \pm x, \quad (5)$$

where $\pm x$ denotes the nonstoichiometry plus impurities. The conservation of charge or electroneutrality may be expressed as follows [44]

$$\sum_q q[\text{X}_d^q] + [\text{h}]_{\text{val}} - [\text{e}]_{\text{con}} = 0. \quad (6)$$

Here, X_d^q is the concentration of defect (vacancy or interstitial) of charge q in site X ($= \text{U}$ or O); and $[\text{h}]_{\text{val}}$ and $[\text{e}]_{\text{con}}$ are the concentrations of holes and electrons in the valence and conduction bands, respectively.

The aforementioned model assumes fixed x , rather than connecting, e.g., the stoichiometry to a relevant thermodynamic quantity, i.e. the chemical potential of oxygen. Moreover, the concentration of divacancies and bound Schottky defects are given by [45]

$$[\text{O}_v\text{U}_v] = [\text{O}_v][\text{U}_v]K_4, \quad (7)$$

$$[\text{O}_v^2\text{U}_v] = [\text{O}_v]^2[\text{U}_v]K_5, \quad (8)$$

where $[\text{O}_v\text{U}_v]$ and $[\text{O}_v^2\text{U}_v]$ are the concentrations of divacancy and bound Schottky trivacancy defects, respectively, and K_4 , K_5 are the corresponding reaction parameters related to the respective binding energies via Arrhenius-type relations. The variables K_1 to K_5 are expressed in terms of the respective defect formation energies E_1 , E_2 , E_3 and binding energies E_4 and E_5 through $K_n = \exp(-E_n/k_B T)$ as noted earlier. Typical numerical values for E_n are listed in Table 1. Henceforth, for the defect formation energies, we use the measured values $E_1 = 3.5$, $E_2 = 9.5$, $E_3 = 6.5$ eV as given in Table 1; and we ignore the contributions of (7) and (8).

From the equations for the oxygen-to-uranium ratio as a function of dopant concentration, as detailed in Appendix A, and the relations in (4),

Table 1: The formation energies (in eV) of various defects in UO_2 : Experiment versus several first-principles computations. The reaction parameter is $K_n = \exp(-E_n/k_B T)$.

Method	E_1	E_2	E_3	E_4	E_5
Experiment [36]	3-4	9.5	6-7	...	...
Mott-Littleton [46]	4.91	19.33	11.47	...	7.40
GGA [47]	3.6	11.8	5.6	...	...
GGA+ U [48]	4.0	14.2	7.2	...	...
GGA+ U [49]	3.95	15.08	7.6	3.67	5.1
LDA+ U [50]	4.26	7.65	1.52	2.15	...

E_1 is the formation energy of oxygen Frenkel pair, E_2 the formation energy of uranium Frenkel pair, E_3 the formation energy of Schottky defect, E_4 the binding energy of uranium-oxygen divacancy pair, E_5 the binding energy of the bound Schottky trivacancy. Here, GGA denotes generalized gradient approximation, LDA local density approximation, and U is the Hubbard model parameter.

the formulas for the concentrations of oxygen and uranium vacancies and interstitials in terms of the dopant concentration can be obtained:

$$[\text{O}_v] = \frac{1}{8} \left[\sqrt{y^2 + 64K_1} \pm y \right], \quad (9)$$

$$[\text{U}_v] = 64K_3 \left[\sqrt{y^2 + 64K_1} \pm y \right]^{-2}, \quad (10)$$

$$[\text{O}_i] = K_1/[\text{O}_v], \quad [\text{U}_i] = K_2/[\text{U}_v]. \quad (11)$$

Here, y is the mole fraction of M_2O_5 or M_2O_3 in UO_2 and the $-$ sign is for the former and the $+$ sign for the latter type of dopant, respectively. The asymptotic values for these quantities are listed in Table 2. Equations (9)-(11) manifestly assume that the associated defects with the dopants are isolated and non-interacting. The dopant concentration dependance of $[\text{O}_v]$, $[\text{O}_i]$, $[\text{U}_v]$, and $[\text{U}_i]$, Eqs. (9)-(11), normalized to $y = 0$, at several temperatures are plotted in Figs. 1 and 2 for M_2O_5 and M_2O_3 type dopants, respectively. It is seen from Fig. 1 that both $[\text{U}_v]$ and $[\text{O}_i]$ will increase with the M_2O_5 concentration and the increase in temperature will reduce these quantities; while the corresponding behaviors of $[\text{U}_i]$ and $[\text{O}_v]$ are vice versa. Furthermore, as can be seen from Fig. 2, the associating trend for the M_2O_3 dopant is opposite. The asymptotic values for finite y (Table 2) provide very good approximations to Eqs. (9)-(11) in the y range of interest.

Figure 1: Normalized (to $y = 0$) molar concentrations of uranium vacancy U_v , uranium interstitial U_i , oxygen vacancy O_v , and oxygen interstitial O_i versus M_2O_5 concentration in $(U,M)O_2$ solid solution at different temperatures according to Eqs. (9)-(11).

Figure 2: Normalized (to $y = 0$) molar concentrations of uranium vacancy U_v , uranium interstitial U_i , oxygen vacancy O_v , and oxygen interstitial O_i versus M_2O_3 concentration in $(U,M)O_2$ solid solution at different temperatures according to Eqs. (9)-(11).

Table 2: Asymptotic values for vacancy and interstitial concentrations in UO_2 with additives.

Limit	$[\text{O}_v]$	$[\text{O}_i]$	$[\text{U}_v]$	$[\text{U}_i]$
Additive M_2O_3		$y \equiv [\text{M}_2\text{O}_3]$		
$y \rightarrow 0$	$K_1^{1/2}$	$K_1^{1/2}$	K_3/K_1	K_1K_2/K_3
y large	$y/4$	$4K_1/y$	$16K_3/y^2$	$(K_2/16K_3)y^2$
Additive M_2O_5		$y \equiv [\text{M}_2\text{O}_5]$		
$y \rightarrow 0$	$K_1^{1/2}$	$K_1^{1/2}$	K_3/K_1	K_1K_2/K_3
y large	$4K_1/y$	$y/4$	$(K_3/16K_1^2)y^2$	$(16K_1^2K_2/K_3)/y^2$

2.2. Diffusion coefficients

According to Lidiard [40], the self-diffusion of U in UO_{2+x} may be related to the defect concentration, i.e. when $x > 0$ it is through U^{4+} vacancies and when $x < 0$ is by U^{4+} interstitials. Since a trivalent oxide additive, in general, makes UO_2 hypostoichiometric, we expect that the uranium diffusion is via the interstitials. On the other hand, a pentavalent oxide additive makes UO_2 hyperstoichiometric, thereby cation diffusion may occur by uranium vacancies. Hence, the uranium or oxygen lattice diffusion coefficient D_L can be related to (or scaled with) the concentration of defects

$$D_L^{\text{U}_v} = D_{\text{U}_v}[\text{U}_v], \quad (12)$$

$$D_L^{\text{O}_v} = D_{\text{O}_v}[\text{O}_v], \quad (13)$$

$$D_L^{\text{U}_i} = D_{\text{U}_i}[\text{U}_i], \quad (14)$$

$$D_L^{\text{O}_i} = D_{\text{O}_i}[\text{O}_i], \quad (15)$$

where, e.g. D_{U_i} is the "intrinsic" diffusion coefficient for uranium interstitials on the uranium sublattice and so on; see e.g. [40, 21, 22, 51]. Substituting now for $[\text{U}_v]$, $[\text{O}_v]$, $[\text{U}_i]$, and $[\text{O}_i]$ from (9)-(11) in (12)-(15), gives the dopant concentration dependent diffusion coefficients in the $(\text{U}_{1-y}, \text{M}_y)\text{O}_{2\pm x}$ compound. The temperature dependence of various intrinsic diffusion coefficients in UO_2 , determined by measurements, has been assessed in the literature [21, 36, 52, 53, 18]. Those used in our subsequent computations are given in Table 3. It is noted that D_{O_v} is about ten orders of magnitude larger than D_{U_i} in the temperature range of interest (1400-2000 K).

Table 3: Diffusivity of point defects in near stoichiometric UO_2 ; $D = D_0 \exp(-Q_D/RT)$.

Point defect	Temperature	D_0	Q_D	Q_D	Source
-	K	m^2/s	J/mol	eV	Experiment
O_v	1466 – 1838	4.4×10^{-8}	48953	0.5	[54]
U_i	1723 – 1973	4.0×10^{-11}	292911	3.0	[40]
U_v	1723 – 1923	1.2×10^{-5}	452000	4.7	[18]
U_v^*	1673 – 1923	2.04×10^{-7}	371600	3.9	[55]
$\text{U}_v^\dagger$	1473 – 1873	2.5×10^{-13}	173675	1.8	[21]

* In $\text{UO}_{2.01}$. † In $\text{UO}_2 + \text{Nb}_2\text{O}_5$.

3. Self-diffusion and creep

It is an empirical fact that the steady state thermal creep rate of UO_2 is strongly affected by the addition of dopants such as Cr_2O_3 and Nb_2O_5 [22, 25]. The steady state creep of oxides with fluorite structure, e.g. UO_2 , ThO_2 , CeO_2 , at high temperatures, typically above $0.4T_m$, where T_m is the melting point, is multifaceted with several mechanisms operative [13, 18, 19]. At high temperatures and low stresses, these polycrystalline oxides deform by stress-directed diffusion through the grains or along grain boundaries. Moreover, both cations and anions diffuse in stoichiometric proportions at steady state. We assume Nabarro-Herring lattice flow, which relates the creep rate to the lattice diffusivity, the inverse of grain area, and the applied stress [13]. More precisely, the creep rate under uniaxial loading is written as

$$\dot{\epsilon} = C_A \frac{\Omega \sigma_a}{k_B T d_g^2} \bar{D}_L. \quad (16)$$

where $\dot{\epsilon}$ is the strain rate, $\Omega = 40.9 \text{ \AA}^3$ the volume of the UO_2 molecule, d_g the grain size, σ_a the applied stress, C_A a material dependent adjustable parameter, and $\bar{D}_L$ the combined diffusion coefficients of the cation and anion acting in parallel [19, 17]

$$\bar{D}_L = \frac{D_L^u D_L^o}{D_L^u + D_L^o}. \quad (17)$$

We should point out that in a polycrystalline UO_2 at lower temperatures, diffusional creep can be a dominant mechanism through the flow of ions in the grain boundary. This flow is called Coble creep, and scales as $\bar{D}_B/d_g^3$ instead of $\bar{D}_L/d_g^2$ of Nabarro-Herring creep; see Sec. 4 for further discussion. Note also that D_L^o and D_L^u can be used for the respective lattice vacancy

and interstitial as given by (13) and (14). In the following two subsections we apply (16) to evaluate experimental results on creep of UO_2 doped with small concentrations of Nb_2O_5 and Cr_2O_3 .

3.1. Creep of UO_2 doped with Nb_2O_5

A systematic work among the early thermal creep studies on UO_2 is the 1981 paper of Sawbridge and coworkers [22], who investigated the creep deformation of UO_2 fuel doped with Nb_2O_5 . They investigated the creep of UO_2 containing small additions of Nb_2O_5 in the stress range 0.5-90 MPa at temperatures between 1422 and 1573 K. Compression creep tests were carried out under a constant load in atmosphere of flowing purified argon. They obtained data on the creep rate of UO_2 with seven dopant concentrations from 0.2 mol% to 1.0 mol% Nb_2O_5 [22]. The samples that they examined had different mean (linear intercept) grain sizes, depicted in Fig. 3(a). It is seen that the grain size steadily increase with Nb_2O_5 concentration until it levels off at a concentration of about 0.5 mole% to $\approx 30 \mu\text{m}$. At high stresses (≥ 70 MPa), Sawbridge et al. found a strong dependence of creep rate on stress, typical of dislocation-controlled creep. At lower stresses (< 70 MPa), a roughly linear dependence on stress, typical of diffusion creep, was observed. As noted in [22], it is in the lower stress regions, typified by a linear stress dependence of creep rate, that the most prominent creep modes occur during normal reactor operating conditions.

Sawbridge et al. [22] used the Nabarro-Herring creep formula with lattice diffusivity like (12) to evaluate their experimental data. However, they do not provide numerical values for the formation energies of the defects nor specify the lattice diffusivity of uranium vacancies. Likewise, they do not explicitly give the full expression for $[\text{U}_v]$, which they supposedly utilize. Since Sawbridge et al.'s database offers a proper benchmark for the model utilized here, we found its reevaluation here quite appropriate.

We have used Eqs. (12), (16), (17) to retrodict the creep rate as a function of Nb_2O_5 concentration and temperature. Note that since $D_L^o \gg D_L^u$, then $\bar{D}_L \approx D_L^u \equiv D_L^{uv} = D_{\text{U}_v}[\text{U}_v]$, and D_{U_v} is specified in Table 3 [21]. The zero dopant concentration limit for $[\text{U}_v] \equiv \text{U}_v(0, T)$ at 1523 K is $K_3/K_2 = 1.182 \times 10^{-10}$, cf. Table 2, which needs to be accounted for by scaling the lattice diffusivity. More explicitly, if y is the dopant concentration, we write

$$D_L^{uv}(y, T) = D_{\text{U}_v}(T) \frac{\text{U}_v(y, T)}{\text{U}_v(0, T)}. \quad (18)$$

Here, we have adjusted the creep factor to $C_A = 5.142$ for the Nb_2O_5 additive. Furthermore, we have assumed an initial impurity level of 3.0×10^{-5} mole fraction. The results of our evaluation are depicted in Fig. 3(b). It is seen from this figure that the calculated creep rates follow the trend of measurements with an overestimation at 0.01 mole fraction of Nb_2O_5 . Nevertheless, our results are comparable to, but not the same as, those calculated by Sawbridge et al. (see figure 11 of [22]). In Fig. 3(b), for the sake of comparison, we have also plotted the results of calculations carried out with constant grain sizes of 15 μm and 30 μm .

3.2. Creep of UO_2 doped with Cr_2O_3

Systematic high-temperature creep rate measurements as a function of temperature and applied stress on doped UO_2 , in particular with Cr_2O_3 additive, are very rare in the open literature, despite its applications in commercial reactor fuel. There is, however, a 1996 experimental study by Dugay et al. [25] on creep of $\text{UO}_2\text{-Cr}_2\text{O}_3$ compound. In more detail, Dugay et al. [24, 25] creep tests were done by compression under argon or reducing (hydrogenated argon) environment at temperatures 1623 to 1923 K on unirradiated specimens. The measurements of creep rate were made under a constant temperature at stresses varying from 20 to 70 MPa. The Cr_2O_3 concentrations of UO_2 specimens were $\{0.0, 0.025, 0.06, 0.1, 0.2\}$ wt%. The grain size as a function of $[\text{Cr}_2\text{O}_3]$ in mole fraction for the specimens are depicted in Fig. 4(a). It was found that Cr_2O_3 additions strongly increase the creep rate relative to that of pure UO_2 in argon atmosphere.

Here, we assume that diffusive creep is governed by the diffusion of uranium interstitials and oxygen vacancies, i.e. we have used equations (13), (14), (16), (17) to retrodict the creep rate as a function of Cr_2O_3 concentration and temperature. However, since the cation diffusivity is much lower than that of anion, only the former will control diffusion-limited deformation, i.e. $D_L^o \gg D_L^u$, then $\bar{D}_L \approx D_L^u \equiv D_L^{u_i} = D_{U_i} U_i$, and D_{U_i} is specified in Table 3. The zero dopant concentration limits for $[U_i] \equiv U_i(0, T)$ at the considered temperatures, cf. Table 2, need to be accounted for by scaling the lattice diffusivity as before

$$D_L^{u_i}(y, T) = D_{U_i}(T) \frac{U_i(y, T)}{U_i(0, T)}. \quad (19)$$

Here, we have selected those data from [25] that seem to be more applicable to uranium/oxygen self-diffusion, i.e., those at temperatures 1573 to 1773

(a)

(b)

Figure 3: (Color online) **(a)** Measured grain size versus Nb₂O₅ mole fraction of UO₂ doped in samples tested by Sawbridge et al. [22]. The broken curve is simply an interpolation through the data points. **(b)** Measured creep rates (circles) vs. calculated values (+) as a function of Nb₂O₅ mole fraction in UO₂ at an applied stress of 20 MPa at 1523 K. Measurements are from [22]. The dashed and dash-dot curves show computations made at constant grain sizes.

K and $\sigma_a = 45$ MPa. To get a good fit of equation (16) to experimental data at the different temperatures, we were compelled to readjust the creep factor C_A accordingly. That is, we used $C_A = 35$, $C_A = 150$ and $C_A = 400$ at $T = 1573$, $= 1673$ and $= 1773$ K, respectively. Furthermore, in order to dampen the computed value of the uranium interstitial concentration at the very low dopant concentration, we assumed an initial dopant concentration value of 3.0×10^{-5} mole fraction as impurity.

The results of our model computations are presented in Fig. 4(b), which compares the measured creep rate values against the calculated ones. Considering the uncertainty in the measurements (up to about $\pm 18\%$) the retrodictions are fairly good. The measured data depicted in Fig. 4(b) are the results of direct fit to the raw data as given in [25].

4. Discussion

In this section a number of factors affecting our model computations of the creep rate are discussed. These include the important input parameters to the model, the mechanisms governing the diffusion controlled creep and the idealization of the model under consideration, i.e. the mass action law.

4.1. Frenkel defect formation energy

A key parameter in our model is the formation energy or enthalpy of the oxygen pair Frenkel defects H_F , here denoted by E_1 , see Table 1. To illustrate this, we have plotted the calculated concentration of the uranium and oxygen vacancies as a function of dopant (M_2O_5) concentration in Fig. 5(a). It is seen that a variation of $3 \leq E_1 \leq 4$ eV makes a large impact on the concentration of the vacancies. This in turn significantly affects the lattice self-diffusion and thereby the creep rate of the fuel, see (16) and (18).

H_F has usually been determined from the oxygen diffusion experiments made on near stoichiometric UO_2 . In more detail, the measured activation enthalpy for oxygen migration in UO_2 is partitioned as $Q = H_v + H_F/2$, where H_v is the anion vacancy migration enthalpy. As noted in [36], different values for H_F will be obtained, depending on whether oxygen vacancies or interstitials are considered to be rate-controlling in the limiting situation of perfect stoichiometry, which is difficult to maintain. Matzke, in several review papers [36, 52, 53], alludes that the experimental values for H_F vary between 3 and 4 eV (Table 1), the source of which is difficult to track down.

(a)

(b)

Figure 4: (Color online) **(a)** Measured grain size versus Cr_2O_3 concentration of UO_2 doped specimens tested in [25]. **(b)** Measured creep rates (filled symbols) vs. calculated values (+) as a function of Cr_2O_3 mole fraction in UO_2 at an applied stress of 45 MPa at different temperatures. Measurements are from [25].

As an example, we should mention the notable paper by Kim and Olander [54], who measured carefully oxygen diffusion in UO_{2-x} using secondary-ion mass spectrometry (SIMS) perpendicular to the diffusion direction. Their data, the normalized diffusivity divided by x and $2 - x$ versus inverse temperature, assuming vacancy mechanism for diffusion, yields $H_v = 48.9 \pm 12.5$ kJ/mol (0.5 ± 0.13 eV). Among the measurements of oxygen diffusion in "nominally stoichiometric" UO_2 , the early data of Marin and Contamin [20] still are considered to be the most reliable, since they span a sufficiently wide range of temperatures (778 to 1247 °C), and were determined by employing a number of *in situ* analytical techniques [56]. Their value for the activation enthalpy is $Q = 248 \pm 21$ kJ/mol (2.6 ± 0.2 eV). Hence, $H_F \approx 4.2$ eV, which is around the upper limit of Matzke's recommendation.

Of course, H_F may be calculated from first principles. Table 1 shows a selected list of values calculated by various density functional theory approximations or DFTs (except [46], which uses the Mott-Littleton approximation). From this table, we see that the GGA result in [47] agrees well with the best estimate value recommended by Matzke, whereas the LDA + U result of Andersson et al. [50] conforms with the aforementioned experimentally determined result taken from [54, 20]. Nevertheless, for H_F , there is a range of values, from 3.6 to 4.9 eV, resulting from various computations. In this connection, we should also mention a recent brief review paper by Dorado et al. [57], which compares various advanced first principles computations of formation energies of neutral point defects in undoped UO_2 .

The discrepancies in the formation energies are striking, especially since it is difficult to decide which one is best, or let alone to give a ballpark value. For example, the formation energies vary from 4.0 to 6.4 eV for oxygen Frenkel pair, from 7.0 to 15.8 eV for uranium Frenkel pair, and from 3.6 to 10.7 eV for Schottky defect. This scatter in the results is unsatisfactory for "accurate" electronic band structure computations. The discrepancies are attributed to the presence of metastable states in UO_2 discussed in [57]. Nevertheless, it shows that modeling accurately actinide-based oxides and their 5f states from first principles is very difficult.

Applying a standard formula from solid state physics, one can relate the energy absorbed by the band structure of UO_2 to the band gap energy E_g and the ratio of the effective and the rest mass of electron m^*/m_e . Kim and Olander [54] using their aforementioned measured data, find $m^*/m_e = 7.6$ and $E_g = 1.95$ eV. The latter is in conformity with X-ray photoemission measurements, which indicate $E_g \approx 2.0$ eV [58]. Moreover, electric conductivity

Figure 5: (Color online) **(a)** Computations of the uranium vacancy concentration (U_v) versus the pentavalent dopant concentration in UO_2 for three values of the Frenkel anion pair energy E_1 at $T = 1573$ K; cf. Table 1 and Fig. 1. **(b)** The corresponding computations of the lattice diffusivity at $E_1 = 3.5$ eV and $T = 1573$ K, per Eq. (18), for three experimental intrinsic diffusivities of U_v : Mat69 [21], Haw68 [55], McN63 attributed to P. McNamara [18]. The associated numerical values of the diffusivity variants (at 1573 K) are: $4.27 \times 10^{-19} m^2/s$ (Mat69), $9.32 \times 10^{-20} m^2/s$ (Haw68), and $1.17 \times 10^{-20} m^2/s$ (McN63); see Table 3.

measurements provide a value for E_g , which is $E_g \approx 2.0$ eV [59].

Regarding the influence of additives, only a few or virtually no experimental studies have been reported in the literature to determine how the particular dopant affect the state of UO_2 at the fundamental level. For example, to see how the ground state properties of UO_2 are altered and thereby in what manner the formation energies of the point defects get affected as a function of dopant concentration. We should, however, mention the early electrical conductivity measurements of Killeen [60], Munir [61] and Matsui & Naito [62] on Nb_2O_5 - and Cr_2O_3 -doped UO_2 and comparisons with that of undoped UO_2 . Such measurements, conducted in a wider range of temperatures and dopant concentrations, will provide valuable data on basic properties of doped UO_2 , which in turn help to elucidate some of the issues raised in the present note.

4.2. *Effective diffusivity*

As noted in Sec. 3, the controlling mechanism for diffusional creep in UO_2 is the diffusion of uranium. As can be seen from Table 3, there is a large disparity between the activation enthalpies of diffusion coefficients reported by various authors in the literature. They vary from 1.8 eV [21], 3.9 eV [55] to 4.7 eV [18] for D_{U_v} and 3.0 eV for D_{U_i} [40]. Plots of the diffusion coefficients (Table 3) versus temperature reveal their overall differences. The D_{U_i} that we have used for creep of Cr_2O_3 -doped UO_2 is lower than the D_{U_v} used for Nb_2O_5 -doped UO_2 [21]. Despite the large difference between the activation enthalpies for D_{U_v} obtained by Matzke [21] and that from Hawkins-Alcock [55], their overall results are not so large. The two relations cross one another at about 1750 K, above which the latter overtakes the former. On the contrary, the D_{U_v} recommended in the atlas by Frost and Ashby and attributed to P. McNamara, which lies central to the UO_2 data assessed by Frost and Ashby [18], is much lower than the other two [21, 55] below 1800 K; see Table 3. Of course, part of this difference can be due to the different impurity levels of the UO_2 samples. In Fig. 5(b), we have plotted the lattice diffusivity according to Eq. (18) as a function of pentavalent dopant concentration using three empirical D_{U_v} variants listed in Table 3 [18, 21, 55]. A point worth mentioning is that in the computations described in Sec. 3.1, we selected D_{U_v} from Matzke's data [21]. We could have chosen very well D_{U_v} from Hawkins-Alcock's data [55]; in that case, the creep factor would have been readjusted to $C_A \approx 35$ to obtain virtually identical results.

In our computations of diffusional creep, we only considered the lattice or volume diffusivity D_L , i.e. the contribution of grain-boundary cation diffusivity D_B (Coble creep) was not taken into account. In general, the effective diffusivity for the Nabarro-Herring-Coble model is expressed as [17, 18, 19]

$$D_{\text{eff}} = D_L \left(1 + \frac{\pi \delta D_B}{d_g D_L} \right). \quad (20)$$

Here, δ is the grain boundary width, which may be taken arbitrarily as 0.554 nm [19]. Disparate values (Arrhenius relations) of D_B for uranium ions in UO_2 have been reported in the literature based on measurements [63, 64, 65]. The data of Alcock et al. [63], which are also recommended in [18], lie between the data of Yajima et al. [64] and the more recent data of Sabioni et al. [65]. These diffusion coefficients as a function temperature differ from one another by several orders of magnitude.

We did attempt to include the relation for δD_B by Alcock et al. [63] into our model for creep computations, i.e. using $\delta D_B = 1.2 \times 10^{-15} \exp(-Q_D/RT)$ in m^3/s with $Q_D = 293 \text{ kJ/mol}$ and (20), because that distorted our output compared with measurements, hence we disregarded its contribution. To resolve the disparity between uranium diffusion data in the lattice and in the grain boundary of UO_2 , new experiments need to be carried out. Note that in the limit $d_g D_L \gg \pi \delta D_B$, D_{eff} tends to the lattice self-diffusivity (Nabarro-Herring creep). This occurs at higher temperatures depending on the grain size, namely the D_{eff} asymptotically converge to the lattice diffusivity D_L at very high temperatures ($> 2000 \text{ K}$) and larger grain sizes ($d_g > 50 \mu\text{m}$).

The mechanisms for uranium self-diffusion in UO_2 are detailed in a recent study by Dorodo et al. [66]. The most likely mechanism was found to be a vacancy mechanism along the $\langle 111 \rangle$ direction and comprises an important influence of the oxygen sublattice. First-principles electronic computations yielded migration barriers of 3.6 eV (GGA + U model) or 4.8 eV (LDA + U model) [66]. These values can be compared with the experimental-based values listed in Table 3, discussed above, or yet with another experimental work by Reimann and Lundy [67], which gave $Q_D = 4.3 \text{ eV}$.

4.3. Effect of temperature and stress

For the Nb_2O_5 additive, the evaluated creep rate data were obtained under an applied stress of 20 MPa at 1523 K [Fig. 3(b)]. For the Nb_2O_5 additive, Fig. 3(b) shows that the model and its parameter settings describe

the data rather well up to a Nb_2O_5 concentration of 0.8 mol%. Beyond this value, the calculation deviates from measurement, namely the calculated value overestimates the creep rate for 1 mol% Nb_2O_5 at the considered stress and temperature. Moreover, it is worthwhile to examine the temperature dependence of creep rate for the Nb_2O_5 additive.

On the other hand, for the Cr_2O_3 additive, the data were obtained under an applied stress of 45 MPa at temperatures 1573 – 1773 K [Fig. 4(b)]. In the latter case, the Nabarro-Herring model and its parameter settings recount the measurements quite well for the Cr_2O_3 concentrations up to 0.35 mol%. That is, both temperature and grain size dependence of creep rate are explicated. To obtain such a good fit, however, we did readjust the creep factor C_A in (16) for each of the evaluated temperatures, i.e. we made C_A to increase with temperature from 1573 K to 1773 K; contrary to the original Nabarro-Herring formula, in which C_A is temperature independent. The functional form of this temperature dependence or its physical origin are presently unknown to us. A more systematic and detailed measurement of creep rate may be needed to resolve the issue or to make our final verdict.

As discussed in Appendix A, the concentrations of uranium vacancy $[\text{U}_v]$ and interstitial $[\text{U}_i]$ are both decreasing functions of temperature, Figs. 1-2. Since these variables enter the lattice diffusivity via (18) and (19), and the creep rate through (16) and (17), the temperature dependence of the latter quantities becomes weaker than in the absence of the considered additives.

Let us now discuss the effect of stress on creep rate. It is well known that several deformation mechanisms are involved in oxides with fluoride crystal structure, in particular UO_2 and ThO_2 [18]. Changes from one mechanism to another manifest as changes of slope on the $\log \dot{\epsilon}$ vs. $\log \sigma$ plot. The actual changes are observed to occur steadily rather than sharply; hence prudence need to be exercised when evaluating data in terms of a single mechanism. Data considered as diffusional creep shall be those for which the grain size dependence of strain rate is verified. At very low stresses, so-called interface-controlled diffusional creep [68, 69] may become important. In that case the strain rate varies as the square of stress, i.e., $\log \dot{\epsilon} \sim 2 \log \sigma$. At higher stresses, dislocation climb and dislocation glide mechanisms will dominate, in which the stress exponent values of the strain rate vary between $n = 3$ and $n = 5$ [19].

A best fit analysis of Sawbridge et al. [22] data on creep of UO_2 doped with Nb_2O_5 indicates that in the stress range of 10 to 50 MPa, for Nb_2O_5 concentrations ranging from 0.1 to 1.0 mol% and temperatures from 1423 to

1523 K, the creep rate is linearly proportional to the applied stress. However, we should mention the experimental work of Ainscough et al. [23] that shows that a transition stress of 20 MPa at 1773 K and an oxygen chemical potential of $\mu_{\text{O}} = -4.5$ eV, at which the creep rate stress exponent for UO_2 -0.4 wt% Nb_2O_5 changes from $n = 1.1$ to $n = 2$. Moreover, these workers found that when the oxygen chemical potential was increased from $\mu_{\text{O}} = -5.8$ eV to -4.5 eV, the strain rate was increased by two orders of magnitude. This was attributed to the formation of Nb^{4+} ion. Over the same range of μ_{O} , the creep activation energy was reduced linearly from 4.4 eV to 2.3 eV. In contrast, the strain rate and activation energy for undoped UO_2 remained almost constant under this change in chemical potential [23].

With the model presented here, we have calculated the temperature/stress dependence of creep rate of UO_2 -0.4 mol% Nb_2O_5 for which a few experimental data are reported in [22]. The results of our calculations together with those of experimental data are presented in Fig. 6. The results up to a stress of 20 MPa are fair, but beyond this stress level, only data for 1453 K are available, which our calculations overestimate.

Figure 6: The variation of creep rate with stress at several temperatures for UO_2 doped with 0.4 mol% Nb_2O_5 . The lines are calculated, whereas the symbols are measured values reported in [22].

Finally, it is worth mentioning that the applied stress, if sufficiently high,

e.g. in the range shown in Fig. 6, can alter the formation/diffusion energies of point defects. However, we are not aware of any experimental study on UO_2 that quantifies or points out its impact. For the effect of homogeneous strain (stress) on the migration energy of vacancies, see e.g. the analyses in [12, 70, 71]. So this effect could yet be another source of uncertainty in the analysis of self-diffusion controlled creep.

4.4. Scope of the model

We have utilized a point defect model based on the mass action law. This approach is valid only at the limit of dilute defect (dopant) concentration, say up to 0.01 mole fraction. At higher defect concentrations, more defects are pressed together, through which the Coulomb interactions among charged species become stronger and the spatial locations of the defects get statistically correlated, i.e. the excluded volume effect becomes important. To this end, a statistical thermodynamic approach may be used [72].

The UO_2 dopants considered here, i.e. Nb_2O_5 and Cr_2O_3 , are commonly utilized to less than 0.01 mole fraction, so the Lidiard point-defect model employed here should remain adequate. But for some other UO_2 additives, such as Gd_2O_3 used as neutron absorber material [73], the concentration level can be quite higher than 0.01 mole fraction, thereby the present model may not be applicable.

Higher dopant concentrations (> 0.01 mole fraction) in UO_2 would also produce other defect configurations, for example, dopant-vacancy clusters. In case of hyperstoichiometry, Willis (2:2:2) defects, each consisting of two oxygen interstitials and an oxygen vacancy, would form [74], whereas in hypostoichiometry, two oxygen vacancies may form a vacancy dimer around U^{3+} ion [75], and also other higher order defects can exist. None of these is considered in the present model.

5. Summary and conclusions

In this paper, the Lidiard point-defect model is extended to express the concentrations of oxygen and uranium vacancies as a function of trivalent and pentavalent oxide dopants. The lattice diffusion coefficients for these defects are then related to the dopant concentrations and temperature. In the case of pentavalent dopant, a hyperstoichiometric situation is assumed, whereas in the trivalent dopant, a hypostoichiometric condition is considered. The input data to the model are the formation energies of the Frenkel pairs and

the Schottky defects, and the diffusion coefficients of oxygen and uranium point defects. These data are taken from measurements reported in the literature. The model should theoretically be adequate for low concentrations of dopants, say ≤ 0.01 mole fraction.

Assuming lattice diffusional flow in the UO_2 solid, the creep strain was related to point-defect diffusivity, thereby to dopant concentration, and also to grain size via the Nabarro-Herring formula. This was used to evaluate previous creep experiments on UO_2 with different concentrations of Nb_2O_5 and Cr_2O_3 . In order to obtain a good fit to the measured data on UO_2 - Cr_2O_3 , in regard to the temperature dependence of creep rate, we found it necessary to make the overall creep factor in the Nabarro-Herring formula temperature dependent.

We have also discussed quantitatively the effects of important parameters to the outcome of the model. These include the uncertainty in the Frenkel formation energy, the lattice cation diffusivity and the role of grain boundary diffusivity in overall diffusivity. The effects of temperature and stress on creep rate were evaluated in light of experimental data. Finally, the scope of the model was discussed. One feature of the putative point defect model is its extreme sensitivity to the Frenkel pair anion formation energy. Namely, a small change, say by about 10% in the formation energy, makes an order of magnitude impact on the concentrations of point defects. Since the formation energies are the necessary input values to the model, their precise values are essential to accurate computations. A similar situation holds for the activation energies of uranium vacancy and interstitial diffusivities in UO_2 . Over these problems, there is a dearth of accurate and systematic data on creep rate versus dopant concentration for the temperature and stress range of interest. Despite these problems, our computations show that creep rate increases exponentially with the dopant concentration, over the practical range of doping, with satisfactory agreement with existing experimental data.

A point worth of deliberation is the source of the temperature dependence of creep rate data, where the conventional Nabarro-Herring model cannot capture. Further theoretical work together with more systematic experimental data may help to resolve this issue. Moreover, contributions of other mechanisms, e.g. dislocation creep may need to be appraised.

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Appendix A. The oxygen to uranium ratios as functions of dopant concentrations

We consider a volume of an ideal lattice containing N_U uranium ions. Then the number of anion sublattice sites N_O is $N_O = 2N_U$. However, not all the lattice sites need to be occupied. If some oxygen ions, N_{Ol} , are on lattice sites and some, N_{Oi} , in interstitial positions, then the mean defect concentrations may be expressed in terms of these quantities

$$[O_v] = \frac{N_O - N_{Ol}}{N_O}, \quad (\text{A.1a})$$

$$[O_i] = \frac{N_{Oi}}{N_O}. \quad (\text{A.1b})$$

The oxygen-to-uranium ratio of the crystal hence can be written as

$$\frac{[O]}{[U]} = \frac{N_{Ol} + N_{Oi}}{N_U} = 2 \frac{N_{Ol} + N_{Oi}}{N_O}. \quad (\text{A.2})$$

Making use of (A.1), we have

$$\frac{[O]}{[U]} = 2(1 + [O_i] - [O_v]). \quad (\text{A.3})$$

Equation (A.3) stems from Eq. (5) of the main text. As in the original model of Lidiard [40], we assume that the dominant terms in (5) are $[O_i]$ and $[O_v]$, i.e. we approximate: $[O_i] \approx [O_v] \pm x$, which corresponds to Eq. (5) of Lidiard [40]. The same assumption or approximation was also made in [22].

Pentavalent oxide M_2O_5 dopant

Let us consider the case of Nb_2O_5 dopant. Doping UO_2 with Nb_2O_5 in a strongly reducing atmosphere, e.g. dry hydrogen, the Nb^{5+} ion in substitutional positions in UO_2 can get rapidly reduced to a stable Nb^{4+} ionization state [22]. But, as the oxygen partial pressure of the environment increases, the niobium ionizes back to Nb^{5+} , when each ion would donate half an oxygen interstitial to matrix lattice. Moreover, when the niobium is in the ionization state Nb^{5+} , the ions act as donor impurities, meaning that they each donate a free electron for any oxygen acceptor impurities produced by the reaction [22]

By virtue of this process the Nb additions neutralize U_i^{5+} ions in the compound. The system is considered to be hyperstoichiometric, for example $\langle U_{1-y}Nb_yO_{2+x} \rangle$. If we denote the pentavalent metal oxide as M_2O_5 ($\equiv Nb_2O_5$), the O/U ratio, in non-reducing conditions, is given as

$$\frac{[O]}{[U]} = \frac{(1 - [M_2O_5])N_O + \frac{5}{2}[M_2O_5]N_U}{N_U}. \quad (A.5)$$

Furthermore, since $N_O = 2N_U$, (A.5) reduces to

$$\frac{[O]}{[U]} = 2 + \frac{1}{2}[M_2O_5]. \quad (A.6)$$

Trivalent oxide M_2O_3 dopant

Introducing a trivalent oxide M_2O_3 , e.g. Cr_2O_3 , in UO_2 , and supposing that the M atoms enter the interstitial sites in the UO_2 lattice; the dopant will be ionized to a trivalency of +3, with the lattice defect equilibrium condition

This reaction is in line with studies of M_2O_3 doping of CeO_2 (isomorphous to UO_2), referred to as vacancy compensation mechanism or VCM [76]. It is pointed out in [76] that the VCM in M_2O_3 -doped CeO_2 is favorable for large cations (say with radii > 0.8 Å). For the smallest dopant cations some compensation through dopant interstitials may occur, though they will be minority defects [76]. Hence, it is plausible to assume that VCM also prevails in Cr_2O_3 -doped UO_2 . This should reduce the concentration of oxygen interstitials and increase that of oxygen vacancies, thereby decreasing the concentration of cation vacancies through the Schottky equilibrium equation (4c) and subsequently increase the concentration of cation interstitials through the Frenkel pairs (4b).

If the system is hypostoichiometric, e.g. $\langle U_{1-y}Cr_yO_{2-x} \rangle$, in a reducing environment, the O/U ratio of the M_2O_3 doped UO_2 may be expressed by

$$\frac{[O]}{[U]} = \frac{(1 - [M_2O_3])N_O + \frac{3}{2}[M_2O_3]N_U}{N_U}. \quad (A.8)$$

Replacing N_O with $2N_U$ in (A.8), we obtain

$$\frac{[O]}{[U]} = 2 - \frac{1}{2}[M_2O_3]. \quad (A.9)$$

The substitution of trivalent dopant cations for U^{4+} creates an oxygen vacancy for every two M^{3+} ions, i.e., for every molecule of M_2O_3 ; as in the case of trivalent doping of CeO_2 [76]

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