EFFECT OF ADDITIVES Nb$_2$O$_5$ AND Cr$_2$O$_3$ ON CREEP OF UO$_2$

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ABSTRACT

The creep of UO$_2$ doped with Nb$_2$O$_5$ or Cr$_2$O$_3$ 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 ion concentrations, which in turn are functions of dopant concentrations. The model has been used to evaluate past creep experiments on doped UO$_2$ that were made as a function of dopant concentration (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 model, after a modification of the creep rate coefficient, retrodict the measured data satisfactorily.

INTRODUCTION

Doping the reactor fuel UO$_2$ with a small amount of certain metal oxides, such as Nb$_2$O$_5$ or Cr$_2$O$_3$, will enhance self-diffusion processes in the fuel considerably during service at sufficiently high temperatures and under sintering in fabrication (Radford, 1983). This effect leads, among others, to a higher fuel creep rate, or more viscoplastic behaviour, during reactor operation, thereby causing a softer fuel pellet contact with the cladding upon pellet-cladding interaction (PCI). Because PCI remains a major technical issue in reactor fuel performance, there is a great motivation to lessen its severity, e.g. by means of fuel doping (see e.g. Howl et al. 1994, Marsh et al. 1996, Nonon et al. 2004). Additives such as Nb$_2$O$_5$ and Cr$_2$O$_3$ also affect other UO$_2$ fuel properties, among them fission product gas behaviour (Massih, 2014).

The relationship between the self-diffusion and creep of UO$_2$ is well-known; see e.g. (Frost and Ashby 1982, Knorr et al. 1989). Particularly, the strong dependence of uranium self-diffusion and creep rate on the oxygen chemical potential in uranium oxide, in which a slight increase in oxygen concentration beyond stoichiometry, leads to a large increase in diffusivity and creep rate (Matzke 1969). The creep of UO$_2$ doped with Nb$_2$O$_5$ 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. (1981). These workers observed that Nb$_2$O$_5$ 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$_2$O$_5$-doped UO$_2$ was investigated by Ainscough et al. (1981), who observed that 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 et al. (1981) associated this effect with the formation of Nb$^{4+}$ ion.

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 (Liu. et al. 2012). Self-diffusion in oxides with fluorite structures and in particular UO$_2$ is controlled by the concentrations of point defects, which

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regulate the oxygen to metal ratio in the material, i.e. the O/U ratio in UO₂. Additives such as Nb₂O₅ and Cr₂O₃ affect the O/U ratio and thereby change the concentration of the point defects.

Here, we consider a point defect model, based on the law of mass action, to relate the concentrations of point defects to that of dopants (Nb₂O₅ and Cr₂O₃) in UO₂. 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 U⁴⁺ vacancies for Nb₂O₅-dopant and via U³⁺ interstitials for Cr₂O₃-dopant. We assume that the lattice Nabarro-Herring diffusional creep mechanism (Ashby 1969) is prevalent over the temperature and stress region of interest for the systems under consideration.

THE POINT-DEFECT AND CREEP MODEL

The considered point-defect model was originally developed by Lidiard (1966) for calculation of self-diffusion of uranium in UO₂ₓ. Here, we adapt this model to the case of metal-oxide additives of type M₂O₃ (pentavalent) and M₂O₅ (trivalent), where M stands for metal, in UO₂. In the Lidiard point-defect model, which can be derived from the law of mass action (see e.g. Hayes and Stoneham 1985), the concentrations of Frenkel and Schottky defects in UO₂ₓ hold as follows

\[
\begin{align*}
[O_v][O_i] &= K_1, \\
[U_v][U_i] &= K_2, \\
[O_v]^+ [U_v] &= K_3,
\end{align*}
\]

(1a) (1b) (1c)

where \([O_v]\) and \([O_i]\) are the concentrations of oxygen vacancies and interstitials, respectively, and so are \([U_v]\) and \([U_i]\) for uranium, \(K_v = \exp(-\beta E_v), \beta = 1/k_B T, \) \(k_B\) is the Boltzmann constant, \(T\) is the absolute temperature, and \(E_v\) is the formation energy for the respective point-defect. Equations (1a) and (1b) are for the oxygen and uranium Frenkel pairs (defects), whereas (1c) is for the Schottky defect. Typical numerical values for \(E_v\) are given in Table 1; we use here \(E_1 = 3.5, E_2 = 9.5, E_3 = 6.5\) eV. In addition, a balance equation for concentration and stoichiometry needs to be satisfied, namely

\[
2[U_v] + [O_v] = 2[U_i] + [O_i] ± x,
\]

(2)

where ±x denotes the nonstoichiometry plus impurities. From the equations for the O/U ratio as a function of dopant concentration (Massih 2015) and the relations in (1a)-(1c), the formulas for the concentrations of oxygen and uranium vacancies and interstitials in terms of the dopant concentration can be obtained:

\[
\begin{align*}
[O_v] &= \frac{1}{8} \left[ \sqrt{y^2 + 64 K_i} ± y \right], \\
[U_v] &= 64 K_i \left[ \sqrt{y^2 + 64 K_i} ± y \right]^2,
\end{align*}
\]

(3) (4)

\([O_v] = K_1 /[O_v]\) and \([U_v] = K_2 /[U_v]\). Here, \(y\) is the mole fraction of M₂O₅ or M₂O₃ in UO₂ and the minus sign is for the former and the plus sign for the latter, respectively. These relations exhibit that both \([U_v]\) and \([O_v]\) will increase with the M₂O₅ concentration and an increase in temperature will reduce both these
quantities; while the corresponding behaviour for $[U_1]$ and $[O_1]$ is vice versa. Furthermore, the associating trend for the $\text{M}_2\text{O}_3$ dopant is the opposite.

Table 1: Formation energies (eV) of the considered point-defects in UO$_2$, see Eqs. (1a)-(1c). Experiment versus several first-principles computations: GGA (generalized gradient approximation), LDA (local density approximation), $U$ stands for the Hubbard model.

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$E_3$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>3.4</td>
<td>9.5</td>
<td>6.7</td>
<td>Matzke (1987)</td>
</tr>
<tr>
<td>Mott-Littleton</td>
<td>4.91</td>
<td>19.33</td>
<td>11.47</td>
<td>Jackson et al. (1987)</td>
</tr>
<tr>
<td>GGA</td>
<td>3.6</td>
<td>11.8</td>
<td>5.6</td>
<td>Freyss et al. (2005)</td>
</tr>
<tr>
<td>GGA+U</td>
<td>4.0</td>
<td>14.2</td>
<td>7.2</td>
<td>Gupta et al. (2007)</td>
</tr>
<tr>
<td>LDA+U</td>
<td>3.95</td>
<td>15.08</td>
<td>7.6</td>
<td>Nerikar et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>4.26</td>
<td>7.65</td>
<td>1.52</td>
<td>Andersson et al. (2011)</td>
</tr>
</tbody>
</table>

According to Lidiard (1966), 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 $x < 0$, it is by $U^{4+}$ interstitials. Since a trivalent oxide additive, in general, makes UO$_2$ hypostoichiometric, we suppose 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 as

$$D_L^{ov} = D_{ov}[U_1],$$

$$D_L^{ov} = D_{ov}[O_1],$$

$$D_L^{mi} = D_{mi}[U_1],$$

where, e.g. $D_{ov}$ is the "intrinsic" diffusion coefficient for oxygen vacancies and so forth; likewise relations can be repeated for the corresponding interstitials. Substituting now for $[U_1]$, $[O_1]$ and $[U_1]$ from Eqs. (3)-(4) etc. in (5a)-(5c) gives the dopant concentration dependent diffusion coefficients in the $(U_{1-x},M_x)\text{O}_{2+x}$ compound. The temperature dependence of the intrinsic diffusion coefficients in UO$_2$ determined by measurements used in our computations are given in Table 2. It is noted that according to the empirical relations in Table 2, $D_{ov}$ is about ten orders of magnitude larger than $D_{li}$ in the temperature range of interest (1400-2000 K).

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 Nb$_2$O$_5$ (Sawbridge et al. 1981) or Cr$_2$O$_3$ (Duguay et al. 1996). 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 (see e.g. Burton 1977, Frost and Ashby 1982, Knorr et al. 1989). 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. Assuming Nabarro-Herring lattice diffusional flow, the creep rate under uniaxial loading can be written as
Table 2: Diffusivity of point defects in near stoichiometric UO$_2$: $D = D_0 \exp(-Q_D / T)$.

<table>
<thead>
<tr>
<th>Point defect</th>
<th>Temperature</th>
<th>$D_0$</th>
<th>$Q_D$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_x$</td>
<td>1466-1838</td>
<td>$4.4 \times 10^{-8}$</td>
<td>5888</td>
<td>Kim-Olander (1987)</td>
</tr>
<tr>
<td>U$_i$</td>
<td>1723-1973</td>
<td>$4.0 \times 10^{-11}$</td>
<td>35229</td>
<td>Lidiard (1966)</td>
</tr>
<tr>
<td>U$_v$</td>
<td>1723-1923</td>
<td>$1.2 \times 10^{-5}$</td>
<td>54363</td>
<td>Frost-Ashby (1982)</td>
</tr>
<tr>
<td>U$_i^*$</td>
<td>1673-1923</td>
<td>$2.04 \times 10^{-7}$</td>
<td>44693</td>
<td>Hawkins-Alcock (1968)</td>
</tr>
<tr>
<td>U$_v^{**}$</td>
<td>1473-1873</td>
<td>$2.5 \times 10^{-13}$</td>
<td>20888</td>
<td>Matzke (1969)</td>
</tr>
</tbody>
</table>

*In UO$_{2.01}$; **In UO$_{2.02}$.

\[
\varepsilon = C_L \frac{\Omega \sigma_a}{k_T d_g^3} \bar{D}_L,
\]

(6)

where $\varepsilon$ is the strain rate, $\Omega = 40.9$ Å$^3$ is the volume of the UO$_2$ molecule, $d_g$ is the grain size, $\sigma_a$ is the applied stress, $C_L$ is a material dependent adjustable parameter, and $\bar{D}_L$ is the combined diffusion coefficients of the cation and anion acting in parallel (Knorr et al. 1989)

\[
\bar{D}_L = \frac{D_{L}^{\alpha} D_{L}^{\beta}}{D_{L}^{\alpha} + D_{L}^{\beta}}.
\]

(7)

In polycrystalline UO$_2$ at somewhat lower temperatures, diffusional creep can be dominated by the flow of ions in the grain boundary. This flow is called the Coble creep, and scales as $D_{L} / d_g^3$ instead of $D_{L} / d_g^2$ as in the Nabarro-Herring creep.

EVALUATION OF CREEP EXPERIMENTS

In the following two subsections, we apply Eqs. (6)-(7) to evaluate experimental results on creep of UO$_2$ doped with small concentrations of Nb$_2$O$_5$ and Cr$_2$O$_3$.

**Creep of UO$_2$ doped with Nb$_2$O$_5$**

A systematic work among the early thermal creep studies is the 1981 paper of Sawbridge and coworkers (1981) who investigated the creep deformation of UO$_2$ fuel doped with Nb$_2$O$_5$ in the stress range of 0.5-90 MPa at temperatures from 1422 to 1573 K. Compression creep tests were carried out under a constant load in atmosphere of flowing purified argon. They provide data on the creep rate of seven dopant concentrations from 0.2 mol% to 1.0 mol% Nb$_2$O$_5$. The samples that were examined had different mean (linear intercept) grain sizes, depicted in Fig. 1A. It is seen that the grain size steadily increases with Nb$_2$O$_5$ concentration until it levels off at a concentration of about 0.5 mol% to ~30 μm. At high stresses (≥70 MPa), Sawbridge et al. (1981) 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 (Sawbridge et al. 1981), it is the lower stress regions, typified by a linear stress dependence of creep rate, in which the most prominent creep modes occur during normal reactor operating conditions.

![Image](image.png)

Figure 1. (A) Measured grain size versus Nb$_2$O$_5$ mole fraction of UO$_2$ doped in samples tested by Sawbridge et al. (1981). (B) Measured creep rates (Sawbridge et al. 1981) versus calculated values (here) as a function of Nb$_2$O$_5$ mole fraction in UO$_2$ at an applied stress of 20 MPa at 1523 K. The dashed and dash-dot curves show computations made at constant grain sizes.

Sawbridge et al. (1981) used the Nabarro-Herring creep formula with lattice diffusivity, as in Eq. (5a), 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 [U$_{\gamma}$], which they have supposedly utilized. Since Sawbridge et al.’s work offers a suitable benchmark for the model used here, we found its reappraisal quite worthwhile.

We have used Eqs. (5a), (6)-(7) to predict the creep rate as a function of Nb$_2$O$_5$ concentration and temperature. Note that since $D^*_{\epsilon} \gg D^*_{\ell}$ then $D_{\ell} = D^*_{\ell} = D^*_{\epsilon} = D_{\epsilon}, [U_{\epsilon}]$, and $D_{\epsilon}$ is specified in Table 2 (Matzke 1966). The zero dopant concentration limit for $[U_{\epsilon}] = U_{\epsilon}(0, T)$ at 1523 K is $K_\ell / K_\epsilon = 1.182 \times 10^{-10}$, which needs to be accounted for by scaling the lattice diffusivity. More explicitly

$$D^e_{\ell}(y, T) = D_{\epsilon}(T) \frac{U_{\epsilon}(y, T)}{U_{\epsilon}(0, T)},$$

(8)

where $y$ is the dopant concentration. Furthermore, in our computations for Nb$_2$O$_5$, we choose $C_\ell = 5.142$ in Eq. (6) and assume an initial impurity level of $3.0 \times 10^{-5}$ mole fraction. The results of our computations together with measurements are depicted in Fig. 1B. 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$_2$O$_5$. Nevertheless, our results are comparable to, but not the same as those reported by Sawbridge et al. (1981). In Fig. 1B 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.
Creep of UO$_2$ doped with Cr$_2$O$_3$

Systematic high-temperature creep rate measurements as a function temperature and applied stress on doped UO$_2$, in particular with Cr$_2$O$_3$ 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. (1996) on creep of UO$_2$-Cr$_2$O$_3$ compound. In more detail, their creep tests were done by compression under argon or reducing (hydrogenated argon) milieu at different temperatures 1623-1923 K on unirradiated specimens. The measurements of creep rate were done under a constant temperature at stresses varying from 20 to 70 MPa. The Cr$_2$O$_3$ concentrations of UO$_2$ specimens were [0.0, 0.025, 0.06, 0.1, 0.2] wt%. The grain size as a function of Cr$_2$O$_3$ in mole fraction for the specimens is depicted in Fig. 2A. Addition of Cr$_2$O$_3$ strongly increases the creep rate relative to that of pure UO$_2$ in argon atmosphere.

![Figure 2](image)

Here, we assume that diffusive creep is governed by the diffusion of uranium interstitials and oxygen vacancies, i.e. we have used Eqs. (5b)-(5c) and (6)-(7) to predict the creep rate as a function of Cr$_2$O$_3$ mole fraction and temperature. However, since the cation diffusivity is much lower than that of anion, only the former will control diffusion-limited deformation, i.e. $D_c^w \gg D_v^w$ then $D_c \approx D_c^w = D_c^w = D_c[U_i]$, and $D_v$ is specified in Table 2 (Lidiard 1966). The zero dopant concentration limits $[U_i] = U_i(0,T)$ at the considered temperatures need to be accounted for by scaling the lattice diffusivity as before

$$D_c^w(y,T) = D_c(U_i(T) \frac{U_i(y,T)}{U_i(0,T)}).$$

(9)

Here, we have selected those data from (Dugay et al. 1996) that seem to be more applicable to uranium/oxygen self-diffusion, i.e., those at temperatures 1573 to 1773 K and $\sigma = 45$ MPa. To get a good fit of Eq. (6) to experimental data at the different temperatures, we were compelled to readjust the creep factor $C_i$ accordingly. That is, we used $C_i = 35$, $C_i = 150$ and $C_i = 400$ at $T = 1573$, $T = 1673$ and $T = 1773$ K, respectively. Furthermore, to dampen the computed value of the uranium interstitial concentration at the very low dopant concentration, as before, we assumed an initial impurity level of $3.0 \times 10^{-5}$ mole fraction.
The results of our model computations are presented in Fig. 2B, which compares the measured creep rate values against the calculated ones. Considering the uncertainty in the measurements (up to about ±18%), the retrodictions are fairly good. The measured data depicted in Fig. 1B are the results of direct fit to the raw data as given in (Duguay et al. 1996).

**DISCUSSION**

**Frenkel defect formation energy**

A key parameter in the putative model is the formation energy or enthalpy of the oxygen pair Frenkel defects $H_F$, here denoted by $E_F$; see Table 1. To illustrate this, we have plotted the calculated concentration of the uranium vacancy as a function of dopant (M$_2$O$_3$ = Nb$_2$O$_3$) concentration in Fig. 3A. It is seen that a variation of $3 \leq E_F \leq 4$ eV makes a large impact on the concentration of the vacancies. This in turn significantly affects the lattice diffusivity and thereby the creep rate of the fuel, see Eqs. (7)-(8).

The value of $E_F = H_F$ (Table 1) can be measured from oxygen diffusion experiments on nearly stoichiometric UO$_2$, which is very difficult to maintain during the experiment (Matzke 1987). Table 1 shows a selected list of values calculated by various density functional theory approximations or DFTs [except Jackson et al. (1987), which use the Mott-Littleton approximation]. From this table, we see that the GGA result (Freysss et al. 2005) agrees well with the best estimate value recommended by Matzke, whereas the LDA + $U$ result of Andersson et al. (2011) conforms with the experimentally determined result of Kim and Olander (1981). Nevertheless for $H_F$, there is a range of values, from 3.6 to 4.9 eV, resulted from various computations.

**Effective diffusivity**

The controlling mechanism for diffusional creep in UO$_2$ is the diffusion of uranium. As can be seen from Table 2, 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 (Matzke 1969), 3.9 eV (Hawkins-Alcock 1968) to 4.7 eV (Frost-Ashby 1982) for $D_{\text{U}}$, and 3.0 eV for $D_{\text{U}}$ (Lidgard 1966). Plots of the diffusion coefficients (Table 2) versus temperature reveal their overall differences. The intrinsic diffusion coefficient $D_{\text{U}}$, that we have utilized for creep of Cr$_2$O$_3$-doped UO$_2$ is lower than the $D_{\text{U}}$, used for Nb$_2$O$_3$-doped UO$_2$ (Matzke 1969). Moreover, despite the large difference between the activation enthalpies for $D_{\text{U}}$, obtained by Matzke (1969) and that from Hawkins-Alcock (1968), 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 $D_{\text{e}}$, recommended by Frost and Ashby is much lower than the other two (Matzke 1969, Hawkins-Alcock 1968) below 1800 K; see Table 2. Part of this difference can be due to the different impurity levels of the UO$_2$ samples. In Fig. 3B, we have plotted the lattice diffusivity according to Eq. (8) as a function of a pentavalent dopant concentration using the three empirical $D_{\text{U}}$, variants listed in Table 2 (Matzke 1969, Hawkins-Alcock 1968, Frost-Ashby 1982).

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 $D_g$ (Coble creep) was not taken into account. Disparate values (Arrhenius relations) of $D_g$ for uranium ions in UO$_2$ have been reported in the literature based on measurements, which are discussed in (Massih 2015).
Figure 3. (A) Computations of the uranium vacancy concentration \(U_v\) versus the pentavalent dopant concentration in \(\text{UO}_2\) for three values of the Frenkel anion pair energy \(E_1\) at \(T = 1573\) K. (B) The corresponding computations of the lattice diffusivity \(D_L\) at \(E_1 = 3.5\) eV and \(T = 1573\) K, per Eq. (8), for three experimental intrinsic diffusivities of \(U_v\): Mat69 (Matzke 1969), Haw68 (Hawkins-Alcock 1968), McN63 attributed to P. McNamara (Frost-Ashby 1982); see Table 2.

**Effect of temperature and stress**

Let us now discuss the effect of stress on creep rate. It is well known that several deformation mechanisms are involved in oxides with fluorite crystal structure, in particular \(\text{UO}_2\) and \(\text{ThO}_2\) (Frost-Ashby 1982). 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 abruptly; therefore caution needs to be exercised when evaluating data in terms of a single mechanism (Knorr et al. 1989). 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 (Burton 1972) may become important. In that case, the strain rate varies as the square of stress, i.e. \(\log \dot{\epsilon} \approx 2\log \sigma\). 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 \(n = 4\) (Knorr et al. 1989).

An analysis of Sawbridge et al. (1981) data on creep of \(\text{UO}_2\) doped with \(\text{Nb}_2\text{O}_5\) indicates that in the stress range of 10 to 50 MPa for \(\text{Nb}_2\text{O}_5\) 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. With the present model, we have calculated the temperature/stress dependence of creep rate of \(\text{UO}_2\)-0.4 mol% \(\text{Nb}_2\text{O}_5\) for which a few experimental data are reported in (Sawbridge et al. 1981). The results of our calculations together with experimental data are presented in Fig. 4. 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.
CONCLUDING REMARKS

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 for 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 \( \leq 0.01 \) mole fraction.

Assuming lattice diffusional flow in the UO\(_2\) solid, the creep strain was related to the 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\(_2\)O\(_5\) and Cr\(_2\)O\(_3\). In order to obtain a good fit to the measured data on UO\(_2\)-Cr\(_2\)O\(_3\), in regard to the temperature dependence of creep rate, we found it necessary to make the coefficient in the Nabarro-Herring formula temperature dependent.

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 drawbacks, 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.

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