Radiation enhanced diffusion processes in UO$_2$ and (U,Pu)O$_2$

E Smirnov and G Elmanov
National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe highway 31, 115409 Moscow, Russia

E-mail: GNElmanov@mephi.ru

Abstract. The diffusion mechanisms and migration characteristics of point defects in the fluorite structures of UO$_2$ and (U, Pu)O$_2$ were analyzed. The possibility of complex migration mechanisms of anionic and cationic vacancy and interstitial Frenkel defects depending on the stoichiometry of materials was shown. The statistical analysis of published data on the radiation-enhanced diffusion (RED) characteristics of metal atoms in UO$_2$ and (U, Pu)O$_2$ for temperatures 1303-1673 K was carried out. An approximate temperature dependence of RED coefficient was obtained. Within the framework of understanding of the mechanisms of diffusion processes in fluorite structure, the approximate temperature dependence of the RED coefficient of oxygen for UO$_2$ and (U, Pu)O$_2$ was proposed.

1. Introduction
Knowledge of characteristics and mechanisms of diffusion processes in UO$_2$ and (U, Pu)O$_2$, particularly in terms of radiation exposure, is useful for a production methods development, as well as for understanding of the processes of radiation damage during operation (such as radiation creep, grain growth, swelling and so on).

The main results of these studies are presented and discussed in the reviews [1-5]. Unfortunately, most of the works have been published a long time ago. This means that these works do not contain any modern analysis of radiation-accelerated diffusion processes in uranium and plutonium oxides. This publication carries out the forecasting parameters of the radiation-accelerated processes of metal atoms diffusion component and oxygen in UO$_2$ and (U, Pu)O$_2$, as well as the analysis of the diffusion processes mechanisms according to the latest published data.

2. Characteristics of diffusion processes in UO$_2$
The low packaging structure density of UO$_2$ (0.65) results in the peculiar characteristics of formation and migration of point defects, as well as the diffusion coefficients of oxygen and metal atoms in UO$_2$ and mixed nuclear fuel (U, Pu)O$_2$.

There were a lot of oxygen diffusion researches in uranium dioxide. It should be noted that the results of these researches were a considerable variation in the measured diffusion parameters of oxygen. It relates to significant differences of techniques applied, as well as to purity and to method of preparing materials, and mostly with abrupt dependence of diffusion characteristics from the stoichiometry of the materials being under research.

Statistical analysis of the experimental data presented in the reviews [1–5] allows us to get for the nominally stoichiometric materials following temperature dependence of the oxygen diffusion coefficients in UO$_2$: 
This is almost with the same as the proposed earlier in work [5] the temperature dependence

\[ D_{O \rightarrow UO_2} = (0.335 \pm 0.065)^{0.22} \exp \left( -\frac{(2.61 \pm 0.11) \text{eV}}{kT} \right) \text{cm}^2/\text{s}. \]  

(1)

However, obtaining reliable data for stoichiometric compositions is complicated by a low possibility of obtaining such materials. Single-phase region of UO\(_2\) compositions is very wide, and an excess of oxygen in the dioxide is difficult to avoid. In this case, reasonable criteria of reliability characteristics of oxygen diffusion processes in nominally stoichiometric compositions UO\(_2\) could be developed through an analysis of diffusion mechanisms.

Assuming that the activation energy for oxygen diffusion is equal to

\[ Q = \frac{1}{2} F + E^m, \]

where \( F \) – a formation energy of oxygen Frenkel defect in the fluorite structure of UO\(_2\), and \( E^m \) – anion energy migration. To estimate \( Q \) we need data on the characteristics of defects in UO\(_2\). The formation energy value of anion Frenkel defect equals to (3.0–4.0) eV [2, 4]. The values of anion migration energy \( E^m \) are different for interstitial and vacancy mechanisms of oxygen diffusion in the UO\(_2\) anion sublattice, and depends on the stoichiometry of oxide. Thus, the activation energy for oxygen diffusion is determined by \( E^m \). This is confirmed by a data scattering in activation energies of oxygen diffusion in UO\(_2\) [2–6] and, accordingly, by an experimental and calculated data on the migration energy of vacancy and interstitial anion Frenkel defects.

The value \( E^m \) for interstitial anion defect equals to (0.8–1.1) eV for the stoichiometric oxide UO\(_2\), and this in the best way is consistent with the above mentioned activation energy of an oxygen diffusion. Indeed, in this case, the activation energy for oxygen diffusion is

\[ Q \approx \frac{1}{2} (3.5 \pm 0.5) + (0.9 \pm 0.1) \approx (2.65 \pm 0.35) \text{eV}. \]

The results of experimental researches of the uranium and actinides diffusion in UO\(_2\) and UO\(_{2+x}\) also demonstrate a very significant impact of stoichiometry. The authors of papers and reviews [2, 4, 5] have proposed the following parameters of the temperature dependence of the uranium diffusion coefficients in quasi-stoichiometry uranium dioxide:

\[ D_{U \rightarrow UO_2} = 0.65 \exp \left( -\frac{5.6 \text{eV}}{kT} \right) \frac{\text{cm}^2}{\text{s}}. \]  

(2)

In accordance with this analysis for the diffusion of uranium in a "quasi stoichiometric" dioxide, it is also proposed the diffusion mechanism with the participation of Frenkel defects, i.e., cation interstitials and vacancies in the cation sublattice.

### 3. Characteristics of radiation-enhanced diffusion in UO\(_2\) and (U,Pu)O\(_2\)

The fundamental characteristics of radiation-enhanced diffusion (RED) metal atoms of U and Pu in UO\(_2\) and (U, Pu) O\(_2\) are of an interest for estimation of the of diffusion processes mechanisms that determine the intensity of radiation damage in the process operation of these materials under irradiation. Unfortunately, in a global experimental practice, the only study of this problem was carried out [7, 8].

Investigations were carried out with the UO\(_2\), (U, 2.5%Pu)O\(_2\) and (U, 1.5%Pu) samples, using \(^{233}\)U and \(^{238}\)Pu in the temperature range (1300–1400) °C in neutron fluxes \((7 \cdot 10^{12} – 1.2 \cdot 10^{14}) \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}\).
during (56–334) hours at fission speeds \( \dot{F} = (7 \cdot 10^{11} f - 6.4 \cdot 10^{13} f) \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \) and doses of
\( F = (4.2 \cdot 10^{17} f - 3.1 \cdot 10^{19} f) \text{ n} \cdot \text{cm}^{-2} \).

The results for temperatures below ~1300 K show that the RED coefficients do not depend on the
temperature (athermal region) and their values are
\[ D^*_{\text{RED}} \approx (5 \pm 9.5) \cdot 10^{-17}, \quad \frac{\text{cm}^2}{\text{s}}. \]

Statistical analysis of the data for the temperature range 1303–1673 K allows to obtain the
approximate temperature dependence of RED for the specified interval, which is of the following form:
\[ D^{U,\text{Pu-UO}_2}_{\text{RED}} \approx (3.62 \pm 29.6) \cdot 10^{-13} \exp \left( \frac{(-1.0 \pm 0.21) \text{eV}}{kT} \right), \quad \frac{\text{cm}^2}{\text{s}}. \]

The results presented by now are unique. Attempts to estimate the coefficients of RED in UO
using computer simulation techniques for low temperatures in the ballistic mixing and high
temperatures cannot be considered being satisfactory, because there is no observed correlation of these
results with experimental data. It is noted [10] that athermal RED in UO at temperatures below 1300
K depends essentially on the behavior of short-lived gaseous fission fragments, and the coefficients of
RED are linearly dependent on the speed of fission. The instant effects of fission are the displaced
atoms and recombining Frenkel pairs [10]. In the case of the dominant recombination process, it can
be assumed that this process is thermally activated. Then the RED coefficient is
\( D^*_{\text{RED}} \sim \sqrt{K_o D_v} \) (\( K_o \) - the generation rate of defects, \( D_v \) - the mobility of vacancies); the migration energy of recombining
defects \( E^d_m \approx 2Q^*_{\text{RED}} \) (\( Q^*_{\text{RED}} \) - activation energy in (2)) [11, 12]. In this case, for the specified
temperature range \( E^d_m \approx 2.0 \pm 0.2 \text{eV} \), and this is consistent with formula for the temperature
dependences of migration of uranium vacancies (\( D^{U\text{O}_2}_{U_v} \)) and interstitials (\( D^{U\text{O}_2}_{U_i} \)) in UO
proposed in [2]:
\[ D^{U\text{O}_2}_{U_v} = 2 \cdot 10^{-3} \exp \left( -\frac{2.4 \text{eV}}{kT} \right), \quad \frac{\text{cm}^2}{\text{s}}; \quad D^{U\text{O}_2}_{U_i} = 1 \cdot 10^{-1} \exp \left( -\frac{2.0 \text{eV}}{kT} \right), \quad \frac{\text{cm}^2}{\text{s}}. \]

Using temperature dependences \( D^{U\rightarrow U\text{O}_2}_{\text{TAD}} \) and \( D^{U\rightarrow U\text{O}_2}_{\text{RED}} \) presented above, where \( D_{\text{TAD}} \) – thermally
activated diffusion coefficient, it is possible to estimate the coefficient of radiation diffusion
enhancement for metal atoms in UO
\( R^{U\rightarrow U\text{O}_2}_{\text{RED}} = \frac{D_{\text{RED}}}{D_{\text{TAD}}} \), which has the following form:
\[ R^{U\rightarrow U\text{O}_2}_{\text{RED}} \approx (5.6 \pm 160) \cdot 10^{-13} \exp \left( \frac{4.6 \pm 1.0 \text{eV}}{kT} \right). \]

Temperature dependence \( R^{U\rightarrow U\text{O}_2}_{\text{RED}} \) in logarithmic representation of reduced temperature is shown in
Figure 1 (line 1):
\[ \log R^{U\rightarrow U\text{O}_2}_{\text{RED}} = -(12.25 \pm 1.32) + (7.46 \pm 1.57) \frac{T_m}{T}, \]
where the melting temperature of UO
\( T_m \approx (3100 \pm 30) \text{ K}. \)

The upper limit of applicability of given expression (6) is determined by a condition of \( R \approx 1, \) for
which \( T \approx (0.61 \pm 0.04)T_m \), that corresponds to the value obtained by statistical processing of all
available data in the publications devoted to RED [13]. The lower limit is determined by the transition
temperature to athermal region. For comparison, figure 1 shows the results of statistical processing of the
coefficients \( R \) for metal elements [13] (line 2).
As follows from the results shown in figure 1, the radiation enhancement of diffusion processes in UO$_2$ is comparable with those for pure metals. The values $T_m/T$ for $R = 1$ corresponds to each other within experimental accuracy.

![Figure 1](https://via.placeholder.com/150)

**Figure 1.** Dependence of coefficient $R_{\text{RED}}$ for U and O in UO$_2$ from temperature:

1. $\text{U} \rightarrow \text{UO}_2$, $(\text{U},\text{Pu})\text{O}_2$ – calculation by the data [7, 8] using the equations (2) and (3):
$$\lg R_{\text{RED}}^{U \rightarrow \text{UO}_2} = -(12.25 \pm 1.32) + (7.46 \pm 1.57) \frac{T_m}{T};$$

2. metals for comparison – according to the data [13]:
$$\lg R_{\text{RED}}^{m} = -(9.70 \pm 0.38) + (5.88 \pm 0.16) \frac{T_m}{T};$$

3. $\text{O} \rightarrow \text{UO}_2$ – according to the data of the present work:
$$\lg R_{\text{RED}}^{O \rightarrow \text{UO}_2} = -(5.73 \pm 0.28) + (3.48 \pm 0.18) \frac{T_m}{T}.$$

Taking into account the diffusion mechanisms, which were mentioned above, and experimental errors presented in this paper, the characteristics of RED anionic defects in UO$_2$ could be predicted.

If we consider that Frenkel pairs are the main defects in the cation and anion sublattices of UO$_2$ and assume consistent ratio of the migration energies of the these defects to the activation energy of thermally activated diffusion of uranium and oxygen in a close-packed structure of UO$_2$, the estimated migration energy of oxygen defects is

$$E_{m}^{\text{def}(O)} \approx E_{m}^{\text{def}(U)} \cdot \frac{Q_{\text{TAD}}^{O \rightarrow \text{UO}_2}}{Q_{\text{TAD}}^{U \rightarrow \text{UO}_2}}, \quad (7)$$

where $E_{m}^{\text{def}(O)}$ and $E_{m}^{\text{def}(U)}$ – migration energies of the oxygen and uranium defects.

Hence, the RED value of oxygen activation energy at the dominant recombination process during the annealing of radiation defects is

$$Q_{\text{RED}}^{O \rightarrow \text{UO}_2} = \frac{1}{2} E_{m}^{\text{def}(O)} \approx \frac{(2.0 \pm 0.2) \cdot (2.61 \pm 0.11)}{2 \cdot 5.6} \approx (0.47 \pm 0.13) \text{ eV}.$$

The value $E_{O}^{m} \sim (1.0 \pm 0.2)$ eV that results from the formula above is consistent with the estimated value of $(0.8-1.1)$ eV, obtained in the papers [2–6].

Taking into account the total value of the ratio $T_m/T$ for $R = 1$, we obtain the expression for the predicted temperature dependence of coefficient of radiation enhancement of oxygen diffusion in UO$_2$

$$R_{\text{RED}}^{O \rightarrow \text{UO}_2} = (1.885 \pm 0.174) \cdot 10^{-6} \exp \left( \frac{(2.14 \pm 0.72) \text{ eV}}{kT} \right). \quad (8)$$

This dependence corresponds to line 3 at figure 1. The real value of this enhancement factor can be significantly lower due to the capture of radiation defects by the fragments of fission in the process of formation of complexes gas atom - defect [5]. Thus, the radiation-enhanced diffusion coefficient of oxygen in UO$_2$ according to (1) and (8) is

$$D_{\text{RED}}^{O \rightarrow \text{UO}_2} = R_{\text{RED}}^{O \rightarrow \text{UO}_2} \cdot D_{\text{TAD}}^{U \rightarrow \text{UO}_2} \approx (6.31 \pm 3.28) \cdot 10^{-7} \exp \left( \frac{(0.47 \pm 0.13) \text{ eV}}{kT} \right) \cdot \frac{\text{cm}^2}{\text{s}}. \quad (9)$$
3. Conclusion

1. The analysis of diffusion mechanisms and point defects characteristics of migration in the fluorite structure UO$_2$ and (U, Pu)O$_2$ was carried out. A possibility of migration mechanisms of anionic and cationic vacancy and interstitial Frenkel defects, depending on the stoichiometry of materials, was demonstrated.

2. Statistical processing of published data on the characteristics of radiation-enhanced diffusion (RED) of metal atoms in UO$_2$ and (U, Pu)O$_2$ was carried out for the temperature range of 1303-1673 K. An approximate temperature dependence of RED coefficient was obtained.

3. Within the knowledge about diffusion processes mechanisms in fluorite structure, an approximate temperature dependence of the RED oxygen in UO$_2$ and (U, Pu)O$_2$ was proposed.

Acknowledgements
This work was performed within the framework of the Center of Nuclear Systems and Materials supported by MEPhI Academic Excellence Project (contract № 02.a03.21.0005, 27.08.2013).

References
[1] Fedorov G and Smirnov E 1984 Diffusion in Reactor Materials (New Delhi: Oxonian Press)
[2] Matzke Hj 1987 Atomic Transport Properties in UO$_2$ and Mixed Oxides (U,Pu)O$_2$ J.Chem. Soc. Faraday Trans. 83 1121–42
[3] Murch G, Richard C, Catlow A Oxygen Diffusion in UO$_2$, ThO$_2$ and PuO$_2$ 1987 J.Chem. Soc. Faraday Trans. 83 1157–69
[4] Matzke Hj 1992 Diffusion Processes in Nuclear Fuels Diffusion Processes in Nuclear Materials Agarwala R (North Holland) 9–69
[5] Matzke Hj 1990 Atomic mechanisms of mass transport in ceramic nuclear fuel materials J. Chem. Soc. Faraday Trans. 86 1243–56
[6] Nagels P, Yan Lierde W and al 1966 Thermodynamics 2 (Vienna) 311–26
[7] Hoh A and Matzke Hj 1973 Fission-enhanced self-diffusion of uranium in UO$_2$ and UC J. Nucl. Materials 48 157–64
[8] Matzke Hj 1983 Radiation enhanced diffusion in UO$_2$ and (U, Pu)O$_2$ Radiation Effects 75 317–25
[9] Martin G, Maillard S, Van Brutzel L and al 2009 A molecular dynamics study of radiation induced diffusion in uranium dioxide J. Nucl. Materials 385 351–57
[10] Matzke Hj, Lucuta P G and Wiss T 2000 Swift heavy ion and fission damage effects in UO$_2$. Nucl. Instr. Methods in Phys. Research B 166-167 920–26
[11] Was Gary S 2007 Fundamentals of Radiation Materials Science (Berlin-Heidelberg: Springer) p 815
[12] Ferry C, Lovera P, Poinssot C and Garcia P 2005 Enhanced diffusion under alpha self-irradiation in spent nuclear fuel J. Nucl. Materials 346 48–55
[13] Smirnov E and Shmakov A 2001 Radiation enhancement of diffusion in metals and alloys Defect and diffusion forum 194-199 (Paris) Diffusion in materials Part 1 pp 1451–56