

Radiation enhanced diffusion processes in UO_2 and $(\text{U,Pu})\text{O}_2$

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Abstract. The diffusion mechanisms and migration characteristics of point defects in the fluorite structures of UO_2 and $(\text{U, Pu})\text{O}_2$ 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 $(\text{U, Pu})\text{O}_2$ 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 $(\text{U, Pu})\text{O}_2$ was proposed.

1. Introduction

Knowledge of characteristics and mechanisms of diffusion processes in UO_2 and $(\text{U, Pu})\text{O}_2$, 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 $(\text{U, Pu})\text{O}_2$, 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 $(\text{U, Pu})\text{O}_2$.

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 :



$$D_{O \rightarrow UO_2} = (0.335 \pm_{0.22}^{0.65}) \exp\left(-\frac{(2.61 \pm 0.11) \text{ eV}}{kT}\right), \frac{\text{cm}^2}{\text{s}}. \quad (1)$$

This is almost with the same as the proposed earlier in work [5] the temperature dependence

$$D_{O \rightarrow UO_2} = 0.26 \exp\left(-\frac{2.6 \text{ eV}}{kT}\right), \frac{\text{cm}^2}{\text{s}}.$$

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

$$Q = \frac{1}{2} E_{FO}^f + E_O^m,$$

where E_{FO}^f – a formation energy of oxygen Frenkel defect in the fluorite structure of UO_2 , and E_O^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_O^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_O^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_O^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:

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

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 $\dot{F} = (7 \cdot 10^{11} f - 6.4 \cdot 10^{13} f) \text{ n} \cdot \text{cm}^{-3} \cdot \text{s}^{-1}$ and doses of $F = (4.2 \cdot 10^{17} f - 3.1 \cdot 10^{19} f) \text{ n} \cdot \text{cm}^{-3}$.

The results for temperatures below ~ 1300 K show that the RED coefficients do not depend on the temperature (athermal region) and their values are

$$D_{RED}^* \approx (5 \pm_{3.2}^{9.5}) \cdot 10^{-17}, \frac{\text{cm}^2}{\text{s}}.$$

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:

$$D_{RED}^{U, Pu \rightarrow UO_2} \approx (3.62 \pm_{3.2}^{29.6}) \cdot 10^{-13} \exp\left(-\frac{(1.0 \pm 0.21) \text{ eV}}{kT}\right), \frac{\text{cm}^2}{\text{s}}. \quad (3)$$

The results presented by now are unique. Attempts to estimate the coefficients of RED in UO_2 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_2 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 $D_{RED}^* \sim \sqrt{K_o D_v}$ (K_o – the generation rate of defects, D_v – the mobility of vacancies); the migration energy of recombining defects $E_m^d \approx 2Q_{RED}^*$ (Q_{RED}^* – activation energy in (2)) [11, 12]. In this case, for the specified temperature range $E_m^d \approx 2.0 \pm 0.2 \text{ eV}$, and this is consistent with formula for the temperature dependences of migration of uranium vacancies ($D_{U_v}^{UO_2}$) and interstitials ($D_{U_i}^{UO_2}$) in UO_2 proposed in [2]:

$$D_{U_v}^{UO_2} = 2 \cdot 10^{-3} \exp\left(-\frac{2.4 \text{ eV}}{kT}\right), \frac{\text{cm}^2}{\text{s}}; \quad D_{U_i}^{UO_2} = 1 \cdot 10^{-1} \exp\left(-\frac{2.0 \text{ eV}}{kT}\right), \frac{\text{cm}^2}{\text{s}}. \quad (4)$$

Using temperature dependences $D_{TAD}^{U \rightarrow UO_2}$ и $D_{RED}^{U \rightarrow UO_2}$ presented above, where D_{TAD} – thermally activated diffusion coefficient, it is possible to estimate the coefficient of radiation diffusion enhancement for metal atoms in UO_2 $R_{RED}^{U \rightarrow UO_2} = \frac{D_{RED}}{D_{TAD}}$, which has the following form:

$$R_{RED}^{U \rightarrow UO_2} \approx (5.6 \pm_{5.2}^{160}) \cdot 10^{-13} \exp\left(\frac{(4.6 \pm 1.0) \text{ eV}}{kT}\right). \quad (5)$$

Temperature dependence $R_{RED}^{U \rightarrow UO_2}$ in logarithmic representation of reduced temperature is shown in Figure 1 (line 1):

$$\lg R_{RED}^{U \rightarrow UO_2} = -(12.25 \pm 1.32) + (7.46 \pm 1.57) \frac{T_m}{T}, \quad (6)$$

where the melting temperature of UO_2 is $T_m \sim (3100 \pm 30) \text{ K}$.

The upper limit of applicability of given expression (6) is determined by a condition of $R = 1$, 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.

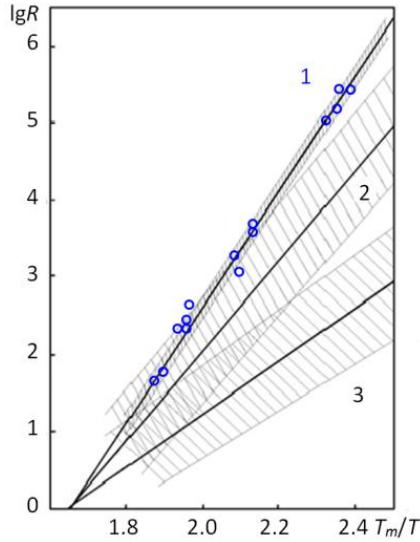


Figure 1. Dependence of coefficient R_{RED} for U и O in UO_2 from temperature:

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):

$$\lg R_{RED}^{U \rightarrow \text{UO}_2} = -(12.25 \pm 1.32) + (7.46 \pm 1.57) \frac{T_m}{T};$$

2 – metals for comparison – according to the data [13]:

$$\lg R_{RED}^{met} = -(9.70 \pm 0.38) + (5.88 \pm 0.16) \frac{T_m}{T};$$

3 – $\text{O} \rightarrow \text{UO}_2$ – according to the data of the present work:

$$\lg R_{RED}^{O \rightarrow \text{UO}_2} = -(5.73 \pm 0.28) + (3.48 \pm 0.18) \frac{T_m}{T}.$$

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

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

where $E_m^{def(O)}$ and $E_m^{def(U)}$ – 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

$$Q_{RED}^{O \rightarrow \text{UO}_2} = \frac{1}{2} E_m^{def(O)} \approx \frac{(2.0 \pm 0.2) \cdot (2.61 \pm 0.11)}{2 \cdot 5,6} \approx (0.47 \pm 0.13) \text{ eV}.$$

The value $E_O^m \sim (1.0 \pm 0.2) \text{ eV}$ that results from the formula above is consistent with the estimated value of $(0.8\text{--}1.1) \text{ eV}$, 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

$$R_{RED}^{O \rightarrow \text{UO}_2} = (1.885 \pm_{0.91}^{1.74}) \cdot 10^{-6} \exp \left(\frac{(2.14 \pm 0.72) \text{ eV}}{kT} \right). \quad (8)$$

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

$$D_{RED}^{O \rightarrow \text{UO}_2} = R_{RED}^{O \rightarrow \text{UO}_2} \cdot D_{TAD}^{U \rightarrow \text{UO}_2} \approx (6.31 \pm_{2.14}^{3.28}) \cdot 10^{-7} \exp \left(-\frac{(0.47 \pm 0.13) \text{ eV}}{kT} \right), \frac{\text{cm}^2}{\text{s}}. \quad (9)$$

3. Conclusion

1. The analysis of diffusion mechanisms and point defects characteristics of migration in the fluorite structure UO_2 and $(\text{U}, \text{Pu})\text{O}_2$ 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 $(\text{U}, \text{Pu})\text{O}_2$ 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 $(\text{U}, \text{Pu})\text{O}_2$ was proposed.

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