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# Post-irradiation fission gas release from high burn-up $UO_2$ fuel annealed under oxidising conditions

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## Abstract

In post-irradiation fission gas release experiments on $UO_2$ fuel, large increases in effective diffusion coefficients have been reported when anneals have been carried out under oxidising conditions. These conditions affect in some way the processes involved in the diffusive phase of gas release associated with the important step of intragranular fission gas transfer to the grain boundaries. The purpose of this paper is to extend a recent model involving fission gas bubble movement to propose a possible explanation. A central part of the model concerns the importance of grain boundaries as a dominant vacancy source. Under normal conditions, boundary concentrations are due to thermal vacancy production but under oxidising conditions, it is suggested that if fast oxygen diffusion takes place along grain boundaries then the subsequent oxidation reaction at the boundary has the potential to cause a huge enhancement of the local vacancy level. As will be demonstrated, an acceleration in the rate of fission gas bubble movement to the grain boundaries will result. A comparison of model calculations with a few selected literature results suggests that the mechanism has more than sufficient strength to give the large effects observed. © 1997 Elsevier Science B.V.

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## 1. Introduction

There have been a number of reports noting the large enhancement of diffusion controlled fission gas release during the post-irradiation or transient annealing of high burn-up $UO_2$ under oxidising conditions [1–4]. In these references, this enhancement is explained in terms of an increase in fission gas diffusion rates allowing faster movement of gas within grains to reach grain boundaries and be released to sample or fuel surfaces. Although this description in terms of fission gas atom diffusion is maybe convenient (and often diffusion coefficients are described as 'effective'), it is worthwhile recalling that the origin of this approach comes from experiments in which the influence of hyperstoichiometry on fission gas release rates were measured after very low irradiation doses [5–7]. For example, the fission gas concentrations in the work of Lindner and Matzke [5] were of the order of $10^{-5}$ at.%. These experiments undoubtedly showed that fission gas diffusion coefficients were indeed greatly increased under oxidising conditions, but a change in the mechanics of the gas release process has been discussed, e.g., [8,9], even after moderate increases of fission gas content, to accommodate the trapping and detrapping of gas atoms from small defects. This is reasonable, but the extrapolation of single gas atom diffusion mechanisms to the annealing of high burn-up $UO_2$ fuel, where the fission gas level (in the region of 1 at.%) is orders of magnitude higher, is far less clear. This is especially so given the very many observations of gas bubble precipitation in such material, e.g., [10–14], particularly the careful study of Cornell [15] showing the precipitation of bubbles from the fission gases left in solution after irradiation. One could also add the absence of positive evidence for thermal resolution [16], and the high solution energies for Kr and Xe in $UO_2$ [17,18].

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In view of the above, there seems to be some merit in describing the fission gas behaviour during annealing of high burn up $UO_2$ samples in terms of gas bubble properties alone. Although it is well established that simple Brownian motion of bubbles is too slow to provide an adequate explanation, the addition of further bubble properties (outlined below) has led to the development of a new model to explain the mechanistics of diffusional fission gas release during post-irradiation annealing [19–21]. The purpose of the present paper is to extend this work to provide a possible explanation for the experimental effects observed when annealing under oxidising conditions.

The basic mechanism and its background has been described in the previous papers so that only the main points will be repeated here. The central argument is that in the release of fission gas during the annealing of high burn-up $UO_2$, the important step in which intergranular gas is moved to grain boundaries can be explained by the strong directed migration of fission gas bubbles that must occur in the vacancy gradient induced between the grain boundary and the original bubbles within the grain. Distances moved by bubbles need not be large; in a spherical grain of radius $R_g$, about 50% of a uniform bubble concentration lies in the layer between $0.8R_g$ and the boundary. From the results of Kashibe et al. [13], there seems to be little doubt that as in metals [22–24], the grain boundaries in $UO_2$ can act as the dominant sources of thermal vacancies during annealing. Equally, there is a strong theoretical basis for the movement of bubbles up the induced vacancy gradient. The recent doubts of Tiwari [25] that direct evidence on this point is lacking have been addressed in Ref. [26]. This reference includes calculations demonstrating that the relevant bubble movement is reflected in the experimental results of Marachov et al. [24] on helium bubbles in nickel.

To ascertain whether the magnitude of the proposed gas release mechanism could be important in practice, and to identify the controlling parameters, a quantitative approach was carried out to simulate bubble behaviour [21]. From the results there appeared to be good agreement between model predictions and the main experimental trends on at least four counts:

(i) the magnitude of measured diffusion coefficients, $D_v$;

(ii) the values of reported gas release fractions and their significant increase with burn up;

(iii) an understanding of reported Booth kinetics (fraction released $\propto (D_v t)^{1/2}/R_g$ at early stages of gas release);

(iv) a quantitative explanation of the Kashibe et al. results [13] showing the evolution of gas bubble size regions in an individual grain during annealing.

Although not highlighted in [21], the influence of grain size as seen in (iii) could be added to this list. Subsequent computer calculations show that the influence of the grain size persists for the whole of the diffusive release period, leading to faster release for smaller grain size.

The approach in Ref. [21] also showed that in the model, the overall gas release process was controlled by two parameters: the volume self-diffusion, $D_v$, dominated the kinetics, apart from the effect of grain size as mentioned above, while the local swelling, $\Delta S$, induced in bringing the original bubbles to their final size, controlled the overall fraction of gas released by the end of the process. The influence of the former parameter was already evident in the equations governing both the interface movement and the bubble movement up the gradient. It is useful to note that by taking into account the ideal gas law and the equilibrium bubble equation, it is easy to show that the swelling, $\Delta S$, is given by the relation $\Delta S \propto G r_b T/\gamma$, where $G$ is the fission gas concentration (the uniform gas fraction remaining after the burst release fraction), $r_b$ is the radii of equilibrium bubbles, and $\gamma$ is the surface energy.

## 2. Extension of the model to annealing under oxidising conditions

From the outline of the model, it is clear that the production of thermal vacancies at the grain boundary is a key element. However, under oxidising conditions, there is a possibility that the production of uranium vacancies at grain boundaries could be greatly enhanced. The mechanism that we propose for this requires that during annealing, fast diffusion of oxygen takes place along grain boundaries. This is not an unusual property for impurities in solids and there is evidence that it occurs in $UO_2$. This comes from the work of Thomas et al. [27,28] who annealed irradiated $UO_2$ in air at 468 K and concluded from the formation of $U_4O_9$ at grain boundaries that there was rapid penetration of oxygen along boundaries to give the observed internal oxidation at boundary sites. This work cannot be used to show that the same grain boundary diffusion must occur at high temperatures under the slightly oxidising conditions relevant to diffusive phase fission gas release. Nevertheless it does suggest that the possibility is not unreasonable and this is the basis on which we proceed. Allowing the oxidation reaction, i.e.,

$$UO_2 + 1/2O_2 \Rightarrow UO_{2+x} \Rightarrow UO_2 + U_v + O_i$$

to take place at grain boundary sites is the next important step since one of the products is a uranium vacancy. Hence the normal thermal vacancy production at the grain boundaries could be augmented under oxidising conditions.

It is particularly important to estimate the vacancy levels induced. Both Lidiard [29] and Griesmeyer and Ghoniem [30] have examined the defect concentrations expected in non-stoichiometric $UO_2$. It can be argued that the uranium vacancy concentration at the boundary should be equal to the steady state level that eventually permeates

Table 1
Grain boundary vacancy concentrations during oxidation as a function of temperature

| Temp. (K) | Degree of hyperstoichiometry, $x$ in $UO_{2+x}$ | | | | | |
|---|---|---|---|---|---|---|
| | $< 10^{-7}$ | 0.0025 | 0.005 | 0.010 | 0.025 | 0.05 |
| 1250 | $4.7 \times 10^{-14}$ | $9.7 \times 10^{-7}$ | $3.9 \times 10^{-6}$ | $1.6 \times 10^{-5}$ | $9.7 \times 10^{-5}$ | $3.9 \times 10^{-4}$ |
| 1500 | $7.8 \times 10^{-12}$ | $1.3 \times 10^{-6}$ | $5.3 \times 10^{-6}$ | $2.1 \times 10^{-5}$ | $1.3 \times 10^{-4}$ | $5.3 \times 10^{-4}$ |
| 1750 | $3.0 \times 10^{-10}$ | $1.7 \times 10^{-6}$ | $6.6 \times 10^{-6}$ | $2.6 \times 10^{-5}$ | $1.6 \times 10^{-4}$ | $6.6 \times 10^{-4}$ |
| 2000 | $4.6 \times 10^{-9}$ | $2.0 \times 10^{-6}$ | $7.8 \times 10^{-6}$ | $3.1 \times 10^{-5}$ | $1.9 \times 10^{-4}$ | $7.8 \times 10^{-4}$ |
| 2250 | $3.9 \times 10^{-8}$ | $2.3 \times 10^{-6}$ | $9.0 \times 10^{-6}$ | $3.6 \times 10^{-5}$ | $2.2 \times 10^{-4}$ | $8.9 \times 10^{-4}$ |
| 2500 | $2.2 \times 10^{-7}$ | $2.9 \times 10^{-6}$ | $1.0 \times 10^{-5}$ | $4.0 \times 10^{-5}$ | $2.5 \times 10^{-4}$ | $9.9 \times 10^{-4}$ |

the whole grain. For the purposes of calculation we thus assume that the uranium vacancy concentration at the grain boundary during the above reaction is that given by Lidiard, i.e.,

$$C_v(U) = (x^2S/F^2)\left[0.5 + (F/x^2) + 0.5(1 + 4F/x^2)^{1/2}\right], \qquad (1)$$

where $F$, the Frenkel energy for the oxygen lattice, and $S$, the formation energy of a Schottky trio, are given by $F = \exp(-Q_f/kT)$ and $S = \exp(-Q_s/kT)$. Griesmeyer and Ghoniem follow Matzke [31] in suggesting values of 3.1 and 6.4 eV respectively for $Q_f$ and $Q_s$ These values are also used here.

In Table 1 the vacancy populations at grain boundaries, calculated with Eq. (1) for different values of x at temperatures between 1250 and 2500 K, are listed together with values of thermal vacancy concentrations ($x < 10^{-7}$).

It is clear that even for small values of $x$, the vacancy level at grain boundaries will be hugely enhanced, with an equally large effect on the value of the vacancy gradient between the boundary and the grain bubbles. In the basic model already discussed this is the only extra feature that needs to be considered to simulate the oxidation conditions of interest. Calculations of the oxidation effect can thus be carried out using the methodology given in a previous paper [21], replacing the thermal vacancy levels at the grain boundaries by those given in Eq. (1) above. A minor change involved the separation of vacancy concentration and vacancy diffusivity which had previously been incorporated into the self diffusion coefficient, $D_v$. In the calculations appropriate to the new conditions, it was necessary to deconvolute $D_v$ and treat the two components separately.

## 3. Model results

With the above approach, calculations have been carried out to illustrate the possible effects of oxidising conditions on fission gas release. In all cases a uranium vacancy migration energy, $E_m$, of 2 eV, a grain radius of 5 μm, and a $\Delta S$ value of 100% has been used. The expression 'fission gas release' is used to indicate the arrival of fission gas bubbles at the grain boundary surface. In order to compare with experimental data, the rapid movement of fission gas along grain boundaries to sample surfaces is tacitly assumed.

To start, isochronal gas release curves have been calculated for a heating rate of 1 K/s, varying the value of $x$ from 0.001 up to 0.1. Results are given in Fig. 1. For the lowest value of $x$, the gas release is controlled almost entirely by the normal thermal vacancy concentration but as $x$ increases there are clearly large downward shifts in release temperatures, moving the release peak by over 1000°. The huge potential of the gas release mechanism under oxidising conditions is clearly demonstrated. However, any exact quantitative prediction should take into account that the results are very sensitive to the values of $Q_f$ and $Q_s$. For example, changing $Q_s$ to 6.8 eV in the Fig. 1 isochronal changed the peak temperature of gas release for $x = 0.1$ from 1500 K to 1800 K. An additional effect could arise from a change in value of $E_m$.

Simulation of isothermal anneals under the same conditions of enhanced grain boundary vacancy production have

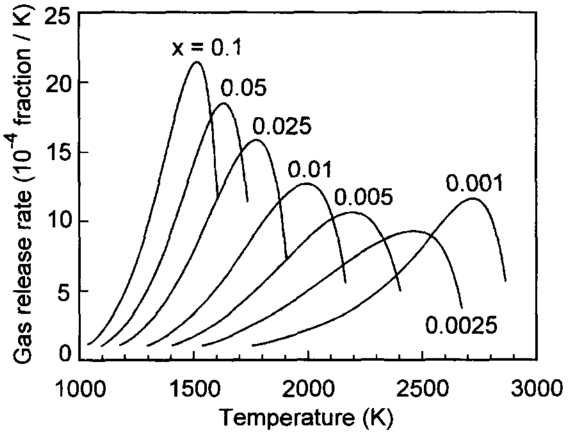

Fig. 1. Computed curves showing the effect of oxidation-induced vacancies at grain boundaries in $UO_{2+x}$ on fission gas release curves during isochronal annealing.

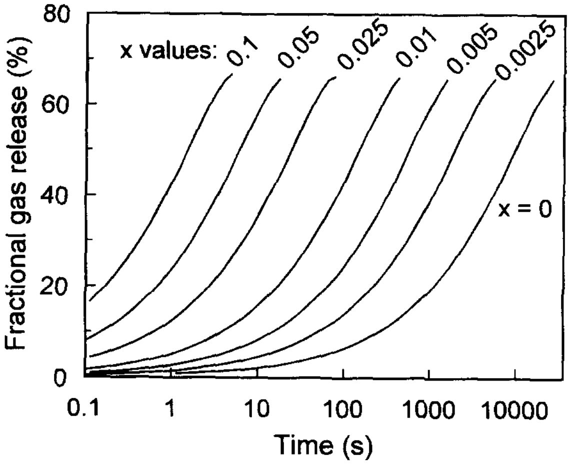

Fig. 2. As for Fig. 1 but for isothermal anneals at 2000 K.

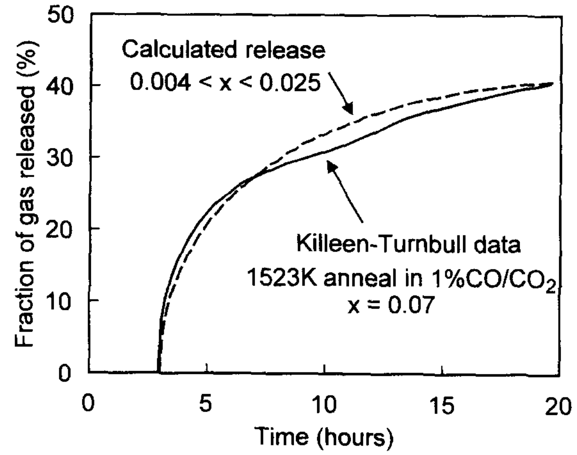

Fig. 3. A calculated fission gas diffusive release curves under oxidising conditions compared with experimental data from Ref. [1]. See text for further details.

also been carried out. These curves, calculated at 2000 K for the same range of $x$ values as in Fig. 1, are shown in Fig. 2. The accelerating effect of high $x$ values is again evident.

In gas release studies, results are often expressed in terms of effective diffusion coefficients. It is easy within the modelling to calculate the influence of the enhanced grain boundary vacancy levels on these coefficients but for convenience this aspect is left until Fig. 4 in Section 4.

## 4. Comparison with experimental data

Although the model curves in Figs. 1 and 2 show large effects, the key question is whether these effects are of the same order as those in the literature. To answer this we examine some selected literature results bearing in mind that straightforward experimental data without the complication of burst release components is limited.

One suitable result appears in the work of Killeen and Turnbull [1]. They showed an experimental diffusive release curve for high burn-up $UO_2$ annealed at 1573 K in an oxidising atmosphere giving conditions equivalent to $x = 0.07$. This is shown in Fig. 3 together with a calculated release curve. The time scale has been left as in the original data, the offset corresponding to the heating period to reach the final anneal temperature. There was no difficulty in fitting the general diffusive form of the experimental curve, with its sharp rise and long tail, using an effective diffusion coefficient of $2 \times 10^{13}$ cm$^2$/s. Within the model, using Eq. (1) and taking $2.0 < E_m < 2.5$ eV, implied a range of $x$ values given by $0.004 < x < 0.025$, considerably less than the estimated experimental value. The relatively large range of $x$ values produced only by a small change in the assumed U vacancy migration energy (keeping $Q_f$ and $Q_s$ as given previously) serves to illustrate the sensitivity of the calculated curves to the input parameters. To emphasise the magnitude of the effects being discussed, it is worth adding that without the extra oxidation vacancies given by Eq. (1), the calculated release of the 35% fission gas fraction in Fig. 3 would have been extended from 20 h to nearly one year.

One conclusion coming from the Fig. 3 comparison was that the calculated effects of annealing in an oxidising atmosphere were larger than required to fit the data. This is also seen in a plot, Fig. 4, comparing diffusion coefficients calculated from the proposed model with selected experimental results under neutral and oxidising atmospheres from the work of Killeen and co-workers [1,12]. The effects of burst release are only briefly mentioned in these papers but it is assumed that it has been accounted for in a consistent way. Although the temperature ranges hardly overlap, the experimental data is useful in illustrating the large effects, a few orders of magnitude, induced by

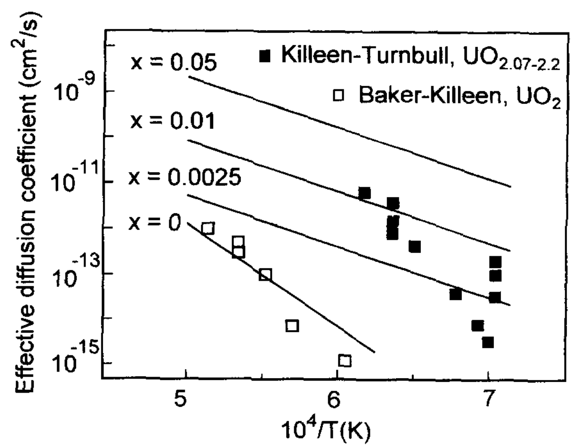

Fig. 4. Calculated diffusion coefficients for the model in text for annealing under different oxidising conditions. Results from Killeen and co-workers [1,12] are shown to illustrate the magnitude of effects found experimentally.

annealing in oxidising atmospheres. (The same large effects are reported by Une et al. [3], although all the effective diffusion coefficients there are a good deal lower, possibly due to a different method of accounting for burst release.) Returning to Fig. 4, it should be mentioned that the derived experimental and calculated diffusion coefficients are model dependent [21] but this is only a very small effect compared to the scale in the figure. As far as the calculated diffusion coefficients are concerned, the $x = 0$ case uses, as in previous work [21], the expression $D_v = 0.3\exp(-4.5/kT)$ cm$^2$/s for the effective $UO_2$ self-diffusion coefficient. For $x > 0$, the calculated diffusion coefficients go in the right direction but clearly overestimate the influence of the value of $x$. Reasonable results could be obtained if both $Q_f$ and $Q_s$ were reduced substantially, e.g., $Q_f = 2$ eV and $Q_s = 4.5$ eV (for $E_m = 2$ eV), but it is not clear if such small values could be realistic.

## 5. Summary

The results presented in this paper show that in the framework of fission gas bubble behaviour, a possible mechanism exists for the enhancement of the diffusive release phase of fission gas release for high burn-up $UO_2$ fuel annealed under post irradiation oxidising conditions. The fact that the proposed mechanism is somewhat too strong in the limited comparison that has been made with experimental results ought not to detract from its applicability; there would be a greater problem were it too weak. Nevertheless, it is recognised that some modification to reduce the predicted effects would be necessary for its quantitative application. Clearly the oxidation reaction at the boundary, and the rate at which it takes place, play a crucial role, and together with the sensitivity of the input parameters could warrant further attention. The remainder of the model is in comparison very straightforward. It is worth emphasising that the proposed mechanism only alters the rate at which grain bubbles move to grain boundaries. All other aspects, such as the dependence of the maximum amount of fission gas fraction released on burnup, and the influence of grain size, will be unchanged from the behaviour predicted in the basic model described previously [21].

Finally, the fact that the basic model can be extended in a relatively straightforward way to accommodate the large reported experimental effects in the special case of annealing $UO_2$ under oxidising atmospheres could add credibility to the overall description of the diffusion phase post-irradiation fission gas release in terms of bubble behaviour.

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