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An advanced model for intragranular bubble diffusivity in irradiated UO_2 fuel

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ABSTRACT

An advanced model for intragranular bubble diffusivity in irradiated UO_2 fuel is developed. Three various (surface, volume and gas-phase) mechanisms for the gas-filled bubbles diffusivity are reconsidered. It is shown that the bubble mobility by the volume diffusion mechanism can be strongly enhanced under irradiation conditions. Influence of the two-phase interface kinetics at a bubble surface on the volume diffusion, evaporation/condensation and surface migration mechanisms that can strongly suppress diffusivity of small nanometre bubbles, is additionally studied using a non-linear adsorption law derived for the van-der-Waals gas in the bubbles. The improved model is implemented in the MFPR code and validated against measurements of the small bubbles mobility.

1. Introduction

The motion of a bubble through a solid essentially requires the transfer of atoms from the leading surface to the trailing surface. Three routes are available to the atoms: they can diffuse around the surface of the bubble (surface mechanism), or through the solid near the bubble (volume mechanism), or via the vapour phase within the bubble (gas-phase mechanism). The bubble mobility is described by the bubble diffusion coefficient which depends on the bubble radius R_b. This dependence is different for the various diffusion mechanisms [1,2]. The bubble mobility in UO_2 is largest for the surface diffusion mechanism (at least for bubbles with $R_b \leqslant 10\ \mu m$) and is inversely proportional to R_b^{-4}, whereas a slower dependence on the bubble radius ($\propto R_b^{-3}$) is typical for the two other mechanisms.

The effect of the internal gas pressure in restricting bubble movement can be very considerable. In the work on helium-filled cavities in nickel [3] it was shown that the gas pressure in small cavities with radius <2.5 nm reduced their mobility to such an extent that it was effectively zero.

For the gas bubbles in UO_2 Baker's data [4] show that small intragranular fission gas bubbles (average diameter ~2 nm), formed during the irradiation were virtually immobile on subsequent annealing at temperatures <1500 °C. With the growth of a bubble radius from 2 to ~10 nm, the bubble diffusivity increases, in contradiction with the standard theoretical predictions.

In order to explain Baker's observations, Mikhlin [5] proposed that a factor which can dramatically affect the surface diffusion mechanism is the presence of a dense gas within the bubble. At the bubble surface a U adsorbed atom (adatom) may not be able to jump into a neighbouring atomic site because such a jump is prevented by adatom interaction with gas atoms [5]. As a result, the net rate of surface diffusion is reduced.

However, in this approach the two other mechanisms (volume and gas phase) of bubble migration become rate controlling steps for small nanometre bubbles and thus do not allow strong reduction of the total diffusivity (in contradiction with Baker's observations). Therefore, additional reasons for reduction of the total bubble diffusivity should be searched.

Such reasons can be apparently associated with faceting of small bubbles observed in the same tests [4]. Indeed, the small intragranular bubble morphology in uranium dioxide irradiated at $T < 1800$ °C was confirmed as octahedron (with faces parallel to {111} with truncation on the {100} planes at the corners), and this was assumed by Baker as a major cause of their immobility. Moreover, noticeable bubble movement has been observed only at annealing temperatures >1700 °C for bubbles of diameter 5–20 nm. At these temperatures the bubbles were spherical.

Earlier Willertz and Shewmon [6] found that faceted helium bubbles in gold diffuse a factor 10^{-4}–10^{-5} slower than theoretically possible from the unrestrained diffusion of surface atoms. On this base, Willertz and Shewmon [6] and Beere [7] have assumed that for faceted bubbles, bubble migration may be limited by the rate at which new steps are nucleated on the facets. It is also known that relocation of steps rather than their nucleation on a crystallographic surface might be a rate controlling process of the surface migration [8]. In both the cases the surface kinetics controlled by the rate at which deposition and solution of atoms occur at the two-phase interface [8] becomes the rate determining step of faceted bubble migration.

In the current paper, the influence of the interface kinetics on the bubble diffusivity mechanisms will be further studied. A special attention will be paid to the effect of the gas pressure in

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restricting small bubbles movement. This will allow explanation of further suppression (in comparison with Mikhlin's mechanism) of the diffusivity of small intragranular bubbles.

In addition, an improved consideration of bubble mobility under irradiation conditions will be presented in the next Section. It is important to note that the formulas for the bubble diffusivities were derived by Shewmon [1] and Nichols [2] for equilibrium conditions. Under irradiation conditions so called a-thermal effects dependent on fission rate might be important. For instance, the effective uranium self-diffusion coefficient may considerably increase under irradiation in UO_2 crystals [9]. Naturally, this can result in the enhancement of the bubble diffusivity. Most pronouncedly this effect can be demonstrated for the bubble volume diffusion mechanism which is directly associated with uranium self-diffusion in the crystal bulk.

2. Bubble diffusivity by volume diffusion mechanism under irradiation conditions

In order to calculate bubble mobility under irradiation conditions, the standard procedure for calculation of bubble mobility in thermally equilibrium crystals (e.g. [10]) should be generalized by additional consideration of non-equilibrium concentration of point defects (vacancies and interstitials).

The components of the stress tensor induced on the bubble surface by an external force $\vec{F}$ exerted on the bubble in the isotropic crystal take the form in the spherical system of coordinates (r, θ, φ) [10]

$$\sigma_{rr}(\theta) = -\frac{3F}{4\pi R_{\rm b}^2}\cos\theta, \quad \sigma_{r\theta}(\theta) = \sigma_{r\varphi}(\theta) = 0 \quad (r = R_{\rm b}), \tag{1}$$

where $\vec{n}$ is the normal to the bubble surface vector, θ is the angle between the vectors $\vec{n}$ and $\vec{F}$, $R_{\rm b}$ is the bubble radius. These stresses induce a force completely compensating the external force:

$$\vec{F}' = \int \sigma_{rr}\cos\theta {\rm d}S \times \frac{\vec{F}}{F} = -\vec{F}.$$

Under conditions of thermodynamic equilibrium on the bubble surface, the chemical potentials of point defects (vacancies and interstitials) $\mu_{v,i}$ connected with their concentrations $c_{v,i}$ at temperature T by the relationship $\mu_{v,i} = \mu_{v,i0} + kT\ln c_{v,i}$, obey the boundary conditions on this surface

$$\mu_v(R_{\rm b}, \theta) = \mu_{v0} + \omega\sigma_{nn} = \mu_{v0} + \omega\sigma_{rr}(R_{\rm b}, \theta), \tag{2}$$

$$\mu_i(R_{\rm b}, \theta) = \mu_{i0} - \omega\sigma_{rr}(R_{\rm b}, \theta), \tag{3}$$

where σ_{nn} are the normal stresses at the bubble surface, ω is the atomic volume of uranium atoms (in the approximation $\omega \approx |\omega_v| \approx |\omega_i|$, see Appendix A), μ_{v0} and μ_{i0} are the equilibrium chemical potentials (normally zero) of vacancies and interstitials, respectively, in the absence of stresses.

Far from the bubble the chemical potentials are determined by the irradiation induced values:

$$\mu_{v,i}(\infty) = \bar{\mu}_{v,i}. \tag{4}$$

In the steady-state approximation the chemical potentials obey the Laplace-type equations:

$$\Delta\mu_{v,i}(\vec{r}) = 0. \tag{5}$$

Solution of Eq. (5) with the boundary conditions (Eqs. (1)–(4)) has the form:

$$\mu_v(\vec{r}) = \bar{\mu}_v - (\bar{\mu}_v - \mu_{v0})\frac{R_{\rm b}}{r} - \frac{3\omega}{4\pi}\frac{\vec{F}\cdot\vec{r}}{r^3}, \tag{6}$$

$$\mu_i(\vec{r}) = \bar{\mu}_i - (\bar{\mu}_i - \mu_{i0})\frac{R_{\rm b}}{r} + \frac{3\omega}{4\pi}\frac{\vec{F}\cdot\vec{r}}{r^3}. \tag{7}$$

The point defect fluxes are determined by the chemical potential gradients, in accordance with relationships:

$$\vec{I}_v = -M_v\vec{\nabla}\mu_v = -\frac{D_v c_v}{\omega kT}\vec{\nabla}\mu_v, \tag{8}$$

$$\vec{I}_i = -M_i\vec{\nabla}\mu_i = -\frac{D_i c_i}{\omega kT}\vec{\nabla}\mu_i, \tag{9}$$

where $M_{v,i}$ are the kinetic coefficients connected with the diffusivities $D_{v,i}$ of vacancies and interstitials by the relationship $D_{v,i} = M_{v,i}\omega kT/c_{v,i}$.

Substitution of Eqs. (6) and (7) in Eqs. (8) and (9) yields:

$$\vec{I}_v = -\frac{D_v c_v}{\omega kT}\left[\frac{3}{4\pi}\left(-\frac{\vec{F}\omega}{r^3} + \frac{\left(\vec{F}\cdot\vec{r}\right)\vec{r}\omega}{r^5}\right) + (\bar{\mu}_v - \mu_{v0})\frac{R_{\rm b}\vec{r}}{r^3}\right], \tag{10}$$

$$\vec{I}_i = -\frac{D_i c_i}{\omega kT}\left[\frac{3}{4\pi}\left(\frac{\vec{F}\omega}{r^3} - \frac{\left(\vec{F}\cdot\vec{r}\right)\vec{r}\omega}{r^5}\right) + (\bar{\mu}_i - \mu_{i0})\frac{R_{\rm b}\vec{r}}{r^3}\right]. \tag{11}$$

Correspondingly, the induced atomic flux is equal to

$$\begin{aligned}\vec{I}_{\rm a} &= -\vec{I}_v + \vec{I}_i \\ &= \frac{(D_v c_v + D_i c_i)}{kT}\left[\frac{3}{4\pi}\left(-\frac{\vec{F}}{r^3} + \frac{(\vec{F}\cdot\vec{r})\vec{r}}{r^5}\right)\right] - \left[D_v(\bar{c}_v - c_v^{(\rm eq)}) - D_i\bar{c}_i\right]\frac{R_{\rm b}\vec{r}}{\omega r^3}.\end{aligned} \tag{12}$$

Migration velocity of a segment of the bubble surface $\vec{v}\prime(R_{\rm b}, \theta)$ can be represented as the sum of the term $\vec{v}$ corresponding to the bubble relocation velocity (as a whole) and of the term $\dot{R}_{\rm b}\vec{n}$ corresponding to the variation of the bubble radius [10]

$$\vec{v}'(R_{\rm b}, \theta) = \vec{v} + \dot{R}_{\rm b}\vec{n}. \tag{13}$$

This velocity obeys the geometrical condition:

$$\vec{v}'(R_{\rm b}, \theta)\cdot\vec{n}(R_{\rm b}, \theta) = \omega\vec{I}_{\rm a}(R_{\rm b}, \theta)\cdot\vec{n}(R_{\rm b}, \theta). \tag{14}$$

Substituting Eq. (12) in Eq. (14) and comparing with Eq. (13), one obtains:

$$\dot{R}_{\rm b} = -[D_v(\bar{c}_v - c_{v0}) - D_i\bar{c}_i]\frac{1}{R_h}, \tag{15}$$

$$\vec{v} = \frac{3\omega}{2\pi}\frac{(D_v c_v + D_i c_i)}{kT}\frac{\vec{F}}{R_{\rm b}^3} = \frac{3\omega}{2\pi}\frac{\widetilde{D}_U}{kT}\frac{\vec{F}}{R_{\rm b}^3}, \tag{16}$$

where $\widetilde{D}_U = D_v c_v + D_i c_i$ is the effective self-diffusion coefficient of uranium atoms (see Appendix A).

It is straightforward to show that in the more general approach, $|\omega_{v,i}| \neq \omega$, with the corrected boundary conditions Eqs. (2) and (3) (as explained in Appendix A), the effective self-diffusion coefficient introduced in Eq. (16) takes the form $\widetilde{D}_U = \gamma_v D_v c_v + \gamma_i D_i c_i$, in correspondence with Eq. (A.9).

Therefore, for the bubble mobility that obeys the relationship $\vec{v} = u_{\rm b}\vec{F}$, one obtains:

$$u_{\rm b} = \frac{3\omega}{2\pi kT}\frac{\widetilde{D}_U}{R_{\rm b}^3}. \tag{17}$$

In accordance with the Einstein equation $D_{\rm b} = kTu_{\rm b}$, the bubble diffusivity is proportional to its mobility and thus can be deduced from Eq. (17) as

$$D_{\rm b}^{(\rm vol)} = \frac{3\omega}{2\pi}\frac{\widetilde{D}_{\rm U}}{R_{\rm b}^3}. \tag{18}$$

Under irradiation conditions the effective self-diffusion coefficient consists of thermal (Arrhenius type) and a-thermal (fission rate dependent) parts [9]

$$\widetilde{D}_{\rm U} = D_{\rm U}^{(0)}\exp(-E_{\rm U}/T) + AG, \tag{19}$$

where $D_U^{(0)} = 2 \times 10^{-4}\ \mathrm{m}^2/\mathrm{s}$, $E_U = 64200$ K, $A \approx 1.2 \times 10^{-39}\ \mathrm{m}^5$ and G is the fission rate.

Correspondingly, for irradiated crystal Eq. (19) should be substituted in Eq. (18). This determines the enhanced bubble diffusivity by volume diffusion mechanism under irradiation conditions.

Simultaneously, Eq. (15) for the bubbles growth rate should be additionally modified taking into account irradiation induced re-solution of gas atoms from bubbles.

3. Influence of the interface kinetics on bubble diffusivity

As explained in Section 1, faceting had pronounced effect in restricting bubble motion in UO_2 crystals.

Qualitatively the observations of faceted bubbles can be explained as suppression by adsorbed gas atoms of so called 'roughening' transition (from smooth (faceted) to rough surface) on UO_2 crystal faces, when gas adsorption coverage is close to 1. The smaller is the bubble, the higher is the gas pressure in the bubble and the closer is gas adsorption to complete coverage; therefore, the transition for small bubbles might be strongly suppressed (i.e. shifted to higher temperatures), in agreement with the above presented Baker's observations [4] that only small bubbles ($\sim$2 nm) had faceted surface (and probably for this reason were immobile, as explained below).

As explained in Section 1, the rate of movement of a bubble with a smooth (faceted) surface may be determined by the rate at which deposition and solution of uranium atoms occur at the two-phase interface. This rate of deposition/solution per unit area can be presented in the general form:

$$W = K_n(\mu_s - \mu_{eq})^n, \tag{20}$$

where K_n is the kinetic ('reaction') constant, μ_s and μ_{eq} are the interface and equilibrium chemical potentials of uranium atoms, respectively. It is customary to take n equal to 1 or 2 [8], however, as proposed in [1], also a larger positive number n can be used to approximate the case in which the cavity are crystallographic and the rate of deposition/solution is determined by the rate of nucleation or growth of atomic steps in the cavity surface.

Under such conditions the bubble diffusivity becomes proportional to the reaction constant K_n and obeys a more slow dependence on bubble radius R_b, as shown in [1]

$$D_b \propto K_n R_b^{n-3}. \tag{21}$$

This slow dependence on R_b results in a noticeable suppression of the mobility for small bubbles (in comparison with the bulk diffusion mechanism which provides $D_b \propto R_b^{-3}$). However, an additional effect can be apparently connected with suppression of K_n for small bubbles with $R_b \sim 1$ nm.

Indeed, in such small bubbles with the surface tension $\gamma \approx 1\ \mathrm{J/m}^2$ the gas pressure is extremely high, $p = 2\gamma/R_b > 1$ GPa, and for this reason, the surface coverage θ of gas atoms adsorbed on the internal bubble surface should be very high, e.g., following the Langmuir adsorption law, $\theta = \frac{k_{ad}p}{1+k_{ad}p} \to 1$. However, this simplest formulation of the adsorption law is valid only for the ideal gas (and at low coverage). For small bubbles with high pressure a new expression for the adsorption isotherm should be derived.

3.1. Non-linear adsorption isotherm

In small bubbles with $R_b \leqslant 5$ nm gas obeys the non-ideal (e.g. van-der-Waals) equation of state: $p(V_b - N_b B) = N_b kT$, where N_b is the number of gas atoms, V_b is the bubble volume and $B \approx 8.5 \times 10^{-29}\ \mathrm{m}^3$/atom is the van-der-Waals constant for Xe gas.

In this case the chemical potential of gas atoms takes the form: $\mu_g = \mu_g^{(0)} + kT \ln p + Bp$, whereas the chemical potential of adsorbed gas atoms is $\mu_{ad} = \mu_{ad}^{(0)} + kT \ln(\theta/(1-\theta))$, where $0 \leqslant \theta \leqslant 1$ is the surface coverage of adsorbed monolayer. This simple expression for μ_{ad} is valid in both limits of $\theta \to 0$ and $\theta \to 1$, when the two-dimensional lattice gas of adatoms (in the case $\theta \to 0$) or of their vacancies (in the case $\theta \to 1$) can be considered as ideal (generally with different values $\mu_{ad}^{(0)}(T)$ and $\tilde{\mu}_{ad}^{(0)}(T)$ in the two limits, respectively). In the current consideration the second case, $\theta \to 1$, is of interest.

In the thermodynamic equilibrium between gas and adsorbed atoms $\mu_{ad} = \mu_g$, therefore, in this case the dependence of the surface coverage on pressure becomes steep and non-linear

$$\theta = \frac{k_{ad} p \exp(Bp/kT)}{1 + k_{ad} p \exp(Bp/kT)}, \tag{22}$$

where $k_{ad} = \exp[(\mu_g^{(0)} - \tilde{\mu}_{ad}^{(0)})/kT]$ is the unknown adsorption constant.

It is clear that under high-coverage condition, $\theta \to 1$, deposition/solution of uranium atoms on the surface will be blocked by adsorbed gas atoms, resulting in a strong suppression of the kinetic constant K_n. In the microscopic consideration of adsorption/desorption processes it is conventionally assumed that K_n is proportional to the surface area unoccupied with gas atoms, $K_n = k_\theta^{(n)}(1-\theta)$, where $k_\theta^{(n)}$ is the second unknown constant of the model, therefore, in the case of the above-derived non-linear adsorption law for small bubbles (with high gas pressure $p = 2\gamma/R_b$), Eq. (22), one obtains:

$$\begin{aligned} K_n &\approx \frac{k_\theta^{(n)}}{1 + k_{ad}(2\gamma/R_b)\exp(2\gamma B/R_b kT)} \\ &\approx (k_\theta^{(n)}/2\gamma k_{ad}) R_b \exp(-2\gamma B/R_b kT). \end{aligned} \tag{23}$$

Therefore, the bubble diffusivity, Eq. (21), can be strongly suppressed for small intragranular bubbles with $R_b \approx 1$ nm owing to extremely small value of the exponent, $\exp(-2\gamma B/R_b\, kT)$, which attains $\approx 10^{-4}$ at $T \approx 1273$ K.

3.2. Bubble diffusivity by volume diffusion mechanism

In order to adequately implement this effect of the bubble mobility suppression, one should self-consistently consider the problem of the bulk self-diffusion in the matrix along with the two-phase interface kinetics at the bubble surface. For the first order kinetics ($n = 1$ in Eq. (20)), the calculations presented in the Appendix B yield for the bubble diffusivity:

$$D_b^{(vol)} = \frac{3\omega}{4\pi R_b^3} \frac{K_1 \omega R_b \cdot 2\widetilde{D}_U}{K_1 \omega R_b + (2\widetilde{D}_U/kT)}. \tag{24}$$

Generalization to the higher order kinetics, $n > 1$, results in

$$D_b^{(vol)} = \frac{3\omega}{4\pi R_b^3} \frac{K_n \omega R_b^n \cdot 2\widetilde{D}_U}{K_n \omega R_b^n + (2\widetilde{D}_U/kT)}, \tag{25}$$

which is correctly reduced to the known relationships in the two limiting cases:

$D_b^{(vol)} \to \frac{3D_U\omega}{2\pi R_b^3}$, when $K_n \omega R_b^n \gg \widetilde{D}_U/2kT$ (the volume diffusion mechanism),

and

$D_b^{(vol)} \to \frac{3K_n\omega^2}{4\pi R_b^{3-n}} kT$, when $K_n \omega R_b^n \ll \widetilde{D}_U/2kT$ (the interface kinetics mechanism).

Substituting Eq. (23) in Eq. (25), one finally obtains:

$$D_b^{(vol)} = \frac{3\omega}{4\pi R_b^3} \frac{(\omega k_\theta^{(n)}/2\gamma k_{ad})\exp(-2\gamma B/R_b kT) R_b^{n+1} \cdot 2\widetilde{D}_U}{(\omega k_\theta^{(n)}/2\gamma k_{ad})\exp(-2\gamma B/R_b kT) R_b^{n+1} + (2\widetilde{D}_U/kT)}. \tag{26}$$

Therefore, for small bubbles the two-phase interface kinetics becomes the rate limiting step in the bubble diffusivity:

$$D_b^{(\mathrm{vol})} \to \frac{3\omega^2 kT}{4\pi R_b^{2-n}}(k_\theta^{(n)}/2\gamma k_{\mathrm{ad}})\exp(-2\gamma B/R_b kT), \tag{27}$$

which tends to 0 when $R_b \to 0$.

3.3. Bubble diffusivity by vaporisation/condensation mechanism

Vaporisation/condensation of UO_2 in the gas-phase provides the interface kinetic limitation to the gas-phase mechanism of bubble diffusivity. This contribution can be represented in the form [11]

$$D_b^{(\mathrm{vap})} = \frac{3\omega^2}{4\pi s^2 k N_b} P_{UO_2(g)} \sqrt{\frac{\pi R}{8mT}}, \tag{28}$$

where N_b is the number of gas atoms in a bubble, k is the Boltzmann constant, R is the universal gas constant, $s = 3.0 \times 10^{-10}$ m and $\pi p s^2$ is the effective cross-section for elastic collisions between Xe atoms and UO_2 molecules, the mass m is defined by $m = m_1 m_2/(m_1 + m_2)$, where m_1 and m_2 are the molar masses of Xe and UO_2. $P_{UO_2(g)}$ is the equilibrium partial pressure of UO_2 gas given by

$$P_{UO_2(g)} = P_0 \exp(-\Delta H_{\mathrm{vap}}/T), \tag{29}$$

where $\Delta H_{\mathrm{vap}} \approx 71.682 \times 10^3$ K is the heat of vaporisation. For small nanometre bubbles N_b is roughly proportional to the bubble volume, therefore, $D_b^{(\mathrm{vap})} \propto R_b^{-3}$.

In a small bubble with high pressure the evaporation/condensation of U atoms will take place from the surface areas unoccupied with gaseous adatoms, therefore, Eq. (28) should be multiplied by the factor $(1 - \theta)$. In the case of the non-linear adsorption law, Eq. (22), for small bubbles (with high gas pressure $p = 2\gamma/R_b$) one obtains:

$$D_b^{(\mathrm{vap})} \approx \frac{3\Omega^2}{4\pi s^2 k N_b} P_{UO_2(g)} \sqrt{\frac{\pi R}{8mT}} \frac{1}{1 + (2\gamma k_{\mathrm{ad}}/R_b)\exp(2\gamma B/R_b kT)}, \tag{30}$$

which tends to 0 when $R_b \to 0$ as

$$D_b^{(\mathrm{vap})} \approx \frac{3\Omega^2}{4\pi s^2 k N_b} \sqrt{\frac{\pi R}{8mT}} P_{UO_2(g)} \frac{R_b}{2\gamma k_{\mathrm{ad}}} \exp(-2\gamma B/R_b kT). \tag{30a}$$

3.4. Bubble diffusivity by surface diffusion mechanism

As mentioned in Section 1, in accordance with Mikhlin's model [5] a U adatom may not be able to jump into a neighbouring atomic site at the bubble surface because such a jump is prevented by adatom interaction with gas atoms.

Under assumption that a U adatom would not diffuse unless a certain volume $V_0 \approx 1.5 \times 10^{-27}\ \mathrm{m}^3$ surrounding the adatom (so called adatom interaction zone) was free of gas atoms, the net rate of surface diffusion is reduced by a factor $(1 - V_0/V_b)^{N_b}$:

$$D_b^{(\mathrm{surf})} = D_s \frac{3\omega^{4/3}}{4\pi R_b^4}\left(1 - \frac{V_0}{V_b}\right)^{N_b} \approx D_s \frac{3\omega^{4/3}}{4\pi R_b^4} \exp\left(-\frac{V_0 P_b}{kT + BP_b}\right), \tag{31}$$

where $P_b = 2\gamma/R_b$ is the bubble pressure, $V_b = 4\pi R_b^3/3$ is the bubble volume, B is the van-der-Waals constant, D_s is the surface self-diffusion coefficient, evaluated in [12] as $D_s = 50 \cdot \exp(-450\,000/RT)$ m^2/s, with 1200 °C < T < 1800 °C and R in $\mathrm{J\,mol^{-1}\,K^{-1}}$.

This approach was criticised in [13], since there is no intrinsic reason why a gas atom in an adatom interaction zone should prevent the adatom from moving, but it has been shown to give results which compare quite favourably with experiments.

An alternative justification for the surface diffusion reduction can be found taking into consideration that atomic jumps into a neighbouring atomic site at the bubble surface can be prevented by occupation of this site by an adsorbed gas atom. Consideration of this mechanism can be carried out by application of the non-linear adsorption law to gas atoms on the bubble surface, similarly to consideration in the previous sections.

Indeed, in this case the U adatom jump frequency on the equilibrium gas bubble surface is less than its jump frequency γ_0 on the free surface, $\gamma_g(r) = \gamma_0 w(r)$, where is the probability that there is a free surface site in the neighbourhood non-occupied with gas atoms, i.e. eventually this results in renormalization of the bubble diffusivity by the same factor $(1 - \theta)$, which can be calculated using the non-linear adsorption law for non-ideal gases, Eq. (22):

$$D_b^{(\mathrm{surf})} = D_s \frac{3\omega^{4/3}}{4\pi R_b^4} \frac{1}{1 + (2\gamma k_{\mathrm{ad}}/R_b)\exp(2\gamma B/R_b kT)}, \tag{32}$$

which tends to 0 when $R_b \to 0$ as

$$D_b^{(\mathrm{surf})} \approx D_s \frac{3\omega^{4/3}}{8\pi\gamma k_{\mathrm{ad}} R_b^3} \exp(-2\gamma B/R_b kT). \tag{32a}$$

4. Model implementation in the MFPR code and validation

New formulations for the bubble volume diffusivity, Eq. (26), and for the vaporization/condensation mechanism, Eq. (30), have been implemented in the MFPR code [14,15] in the form:

$$D_b^{(\mathrm{vol})} = \frac{2\tilde{D}_U\omega}{V_b}\left(1 + \frac{2\tilde{D}_U}{kT\omega}\frac{1}{k_\theta^{(n)}R_b^n}\frac{2\gamma k_{\mathrm{ad}}}{R_b}\exp(2\gamma B/R_b kT)\right)^{-1}, \tag{33}$$

$$D_b^{(\mathrm{vap})} \approx \frac{3\Omega^2}{4\pi s^2 k N_b} P_{UO_2(g)} \sqrt{\frac{\pi R}{8mT}} \frac{1}{1 + (2\gamma k_{\mathrm{ad}}/R_b)\exp(2\gamma B/R_b kT)}, \tag{34}$$

where V_b is the bubble volume, N_b is the number of gas atoms in the bubble, $\tilde{D}_U$ is the effective self-diffusion coefficient of uranium atoms, Eq. (19); the constants $k_\theta^{(n)}$ and k_{ad} are the model parameters, determined below by fitting calculations to the available data on small bubbles diffusivity as $10^{45}\ (\mathrm{N\,m^3\,s})^{-1}$ and $10^{-4}\ \mathrm{m^2/N}$, respectively.

Comparison of the standard volume diffusivity of bubbles $D_b^{(\mathrm{vol})} = 2D_U\omega/V_b$, which includes only the thermal part of the uranium self-diffusion coefficient $D_U = D_U^{(0)}\exp(-E_U/T)$ and thus is valid only for non-irradiation conditions, with the modified one expressed by Eqs. (33) and (19), is presented in Fig. 1. One can see that for bubbles with $R_b > 2$ nm the modified value of the

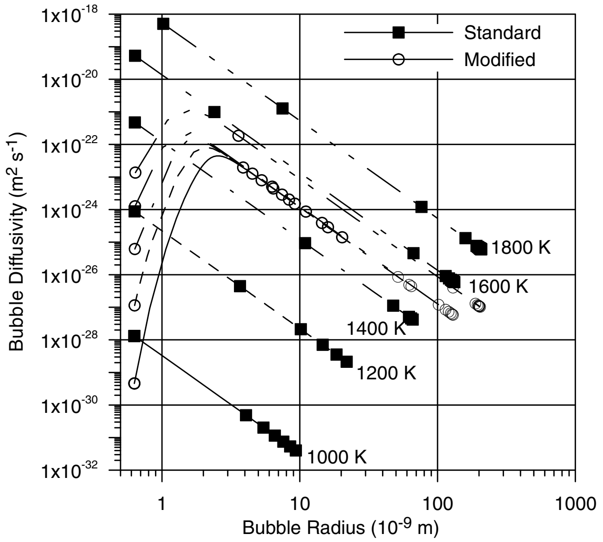

Fig. 1. Volume bubble diffusivity as a function of bubble radius at different temperatures calculated by different models: the standard formulation and the modified model for the irradiation-enhanced bubble diffusivity with consideration of the interface kinetic limitation.

bubble volume diffusivity calculated under irradiation conditions (with the typical fission rate $\sim 10^{19}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1}$) practically does not depend on temperature at $T \leqslant 1400$ K and noticeably exceeds the standard value (especially at low temperatures). At higher temperatures $T \geqslant 1600$ K the thermal part of the uranium self-diffusion coefficient exceeds the a-thermal part and the modified volume diffusivity practically coincides with the standard one. Consideration of the interface kinetic limitation in the new model provides considerable suppression of the volume diffusivity for small bubbles with $R_b \leqslant 2$ nm.

Similarly, modification of the vaporization/condensation model taking into account suppression by gas atoms adsorbed on the bubble surface, Eq. (34), diminishes the bubble diffusivity by this mechanism for small bubbles, Fig. 2.

The surface diffusion mechanism was considered in two formulations: the standard Mikhlin's model, Eq. (31), and the modified model, Eq. (32), as presented in Fig. 3.

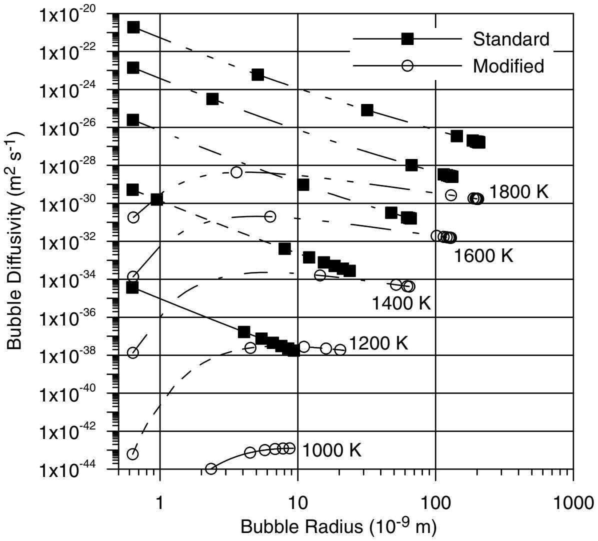

Fig. 2. Vaporization/condensation bubble diffusivity as a function of bubble radius at different temperatures calculated with and without consideration of gas adsorption.

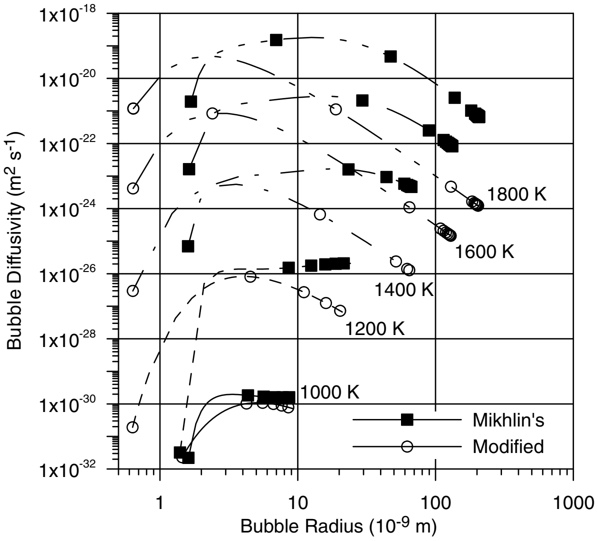

Fig. 3. Surface bubble diffusivity under irradiation conditions as a function of bubble radius at different temperatures calculated by different models: the standard Mikhlin's formulation, Eq. (31), and the modified model, Eq. (32).

Superposition of the diffusion mechanisms allows calculation of the total bubble diffusivity, Fig. 4. In the case of the standard Mikhlin's formulation for the surface diffusion mechanism, Fig. 4(a), results can be well fitted to Baker's [4] and Cornell's [16] data, however, are inconsistent with Gulden's data [17], as shown in Fig. 5. In the case of the modified formulation Eq. (32), Fig. 4(b), coincidence is not so good with Baker's and Cornell's data, however, the calculation results are in much better qualitative agreement with Gulden's measurements (and are still in the range of discrepancy between the three data sets), Fig. 5.

It is important to note from Figs. 1–3 that at temperatures below 1200 K under irradiation conditions with typical fission rates ($\sim 10^{19}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1}$) the irradiation-enhanced volume diffusivity becomes higher than the bubble diffusivity by the surface mechanism and thus determines the diffusivity of intragranular bubbles. This is important conclusion for analysis of bubbles coalescence and UO_2 fuel swelling under normal operation conditions, especially at the fuel pellets periphery where low temperature conditions are sustained.

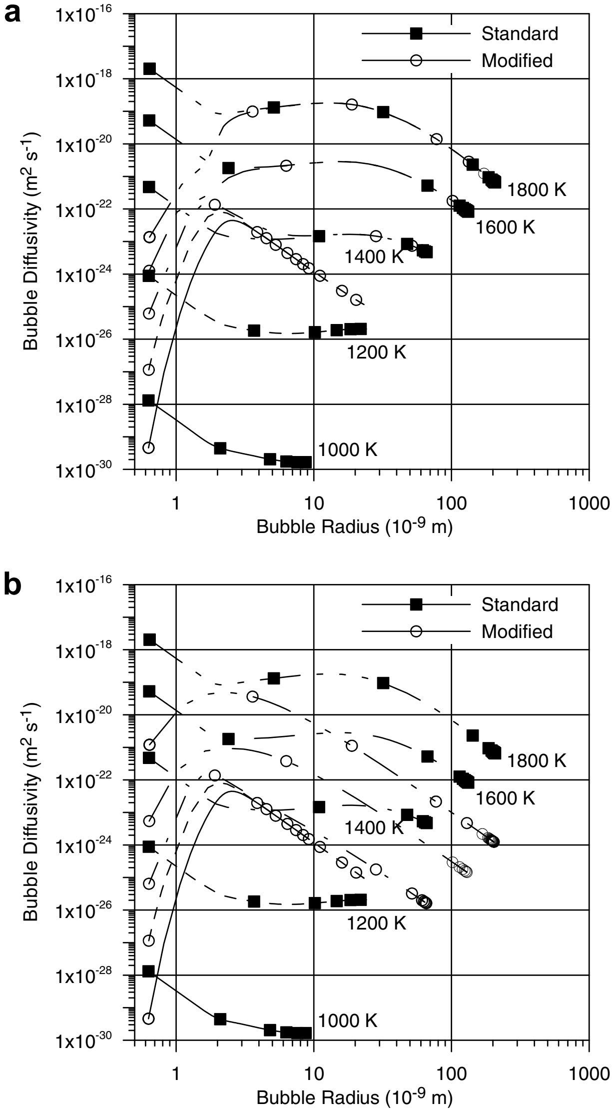

Fig. 4. Total bubble diffusivity as a function of bubble radius at different temperatures calculated with and without consideration of the interface kinetics; (a) using Mikhlin's formulation for the surface diffusion mechanism; (b) using modified formulation, Eq. (32).

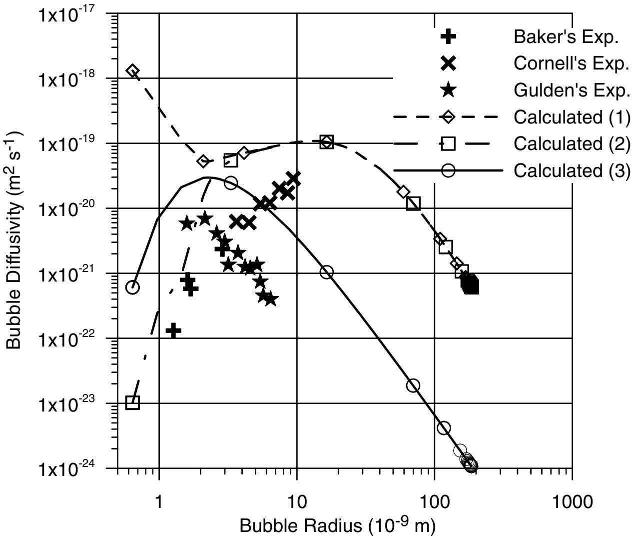

Fig. 5. Total bubble diffusivity as a function of bubble radius at 1773 K experimentally measured and calculated without (dashed line 1) and with consideration of the interface kinetics; for the latter case two options for the surface diffusion mechanism are presented: Mikhlin's formulation, Eq. (31) (dashed-dotted line 2) and modified formulation, Eq. (32) (solid line 3).

5. Conclusions

The advanced model for intragranular bubble diffusivity in irradiated UO_2 fuel was developed. Three various mechanisms (surface, volume and gas-phase) for the gas-filled bubble diffusivity were considered.

It was shown that the bubble mobility by the volume diffusion mechanism can be strongly enhanced under irradiation conditions, in comparison with the standard consideration valid for equilibrium conditions. For instance, at relatively low temperatures $\leqslant$1200 K and typical fission rates ($\sim 10^{19}$ m^{-3} s^{-1}) the volume diffusion mechanism becomes the largest one and thus determines mobility of intragranular bubbles.

The influence of the interface kinetics on bubble diffusivity by volume diffusion, evaporation/condensation and surface diffusion mechanisms was additionally studied. A special attention was paid to the effect of the internal gas pressure in restricting small bubbles movement. For this case a new expression for the non-linear adsorption isotherm for gas atoms was derived. This allowed explanation of further suppression (in comparison with Mikhlin's model for the bubble migration mechanism by surface diffusion) of the diffusivity of small intragranular bubbles.

The standard Mikhlin's model was critically analysed and modified, using the non-linear adsorption isotherm.

The improved models for various mechanisms of the bubble diffusivity were implemented in the MFPR code and applied to analysis of Baker's, Cornell's and Gulden's measurements of small nanometre bubbles mobility. New unknown model parameters characterising the interface kinetic processes were determined by fitting the MFPR calculations to the experimental data.

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Appendix A

Let us consider behaviour of atoms and point defects in crystal under hydrostatic stress field $\sigma_{ii}(\vec{r}) = -P(\vec{r})$. In the case of a homogeneous field, $P = P_0 = \text{const.}$, the equilibrium chemical potentials of point defects can be calculated as

$$\mu_{v,i} = \mu_{v,i0} - \omega_{v,i} P_0, \tag{A.1}$$

where $\omega_{v,i} = \pm\gamma_{v,i}\omega$ is the increase of the crystal volume when one defect is introduced in the crystal bulk by relocation of an atom to (from) the crystal surface; $\gamma_{v,i} = |\omega_{v,i}|/\omega$ normally $\leqslant 1$. Indeed, in this case to attain the equilibrium state the reversible work connected with the crystal volume increase under the external stress, $-\omega_{v,i}\,P_0$, has to be compensated by the chemical potential of the newly created point defect, $\mu_{v,i}$.

It is worthwhile to note that a similar consideration of the equilibrium boundary conditions on the bubble surface will modify the usual Eqs. (2) and (3) (obtained under simplified assumption $\gamma_v \approx \gamma_i \approx 1$) by substitution of $|\omega_{v,i}|$ instead of ω in the right hand side of Eqs. (2) and (3), respectively (or, equivalently, by multiplication of ω by $\gamma_{v,i}$).

In the case of spatially non-homogeneous field with a constant gradient $\vec{\nabla}P = \text{const.}$, $\sigma_{ii}(\vec{r}) = -P(\vec{r}) = -P_0 + \vec{r}\cdot\vec{\nabla}P$, under steady state conditions the chemical potentials of point defects obey the Laplace-type equation:

$$\Delta\mu_{v,i} = 0, \tag{A.2}$$

which has the solution, generalizing Eq. (A.1):

$$\mu_{v,i} = \mu_{v,i0} - \omega_{v,i} P(r). \tag{A.3}$$

Therefore, the point defects diffusion fluxes are calculated as

$$\vec{I}_{v,i} = -M_{v,i}\vec{\nabla}\mu_{v,i} = M_{v,i}\omega_{v,i}\vec{\nabla}P = \pm M_{v,i}|\omega_{v,i}|\vec{\nabla}P = \pm\frac{D_{v,i}c_{v,i}\gamma_{v,i}}{kT}\vec{\nabla}P, \tag{A.4}$$

where $D_{v,i} = M_{v,i}\omega_a kT/c_{v,i}$ is the diffusivity of vacancies (interstitials).

Assuming that the pressure gradient is small, the Gibbs potential of the crystal in a local volume V (with a number of atoms N) can be decomposed at fixed temperature as

$$\Phi(P,T) \approx \Phi(P_0,T) + (P - P_0)V,$$

taking into consideration that $\mathrm{d}\Phi = -S\mathrm{d}T + V\mathrm{d}P$, where S is the entropy.

In this case, for the atomic chemical potential one obtains:

$$\mu_a = \frac{\partial\Phi(P,T)}{\partial N} \approx \frac{\partial\Phi(P_0,T)}{\partial N} + (P - P_0)\frac{\partial V}{\partial N} = \mu_{a0} + (P - P_0)\omega, \tag{A.5}$$

thus, the atomic flux is calculated as:

$$\vec{I}_a = -M_a\vec{\nabla}\mu_a = -M_a\omega\vec{\nabla}P, \tag{A.6}$$

or, in accordance with the Einstein equation for the self-diffusion, $M_a = D_a/\omega kT$:

$$\vec{I}_a = -\frac{D_a}{kT}\vec{\nabla}P. \tag{A.7}$$

On the other hand,

$$\vec{I}_a = -\vec{I}_v + \vec{I}_i, \tag{A.8}$$

therefore, substituting Eqs. (A.4) and (A.7) in Eq. (A.8), one obtains:

$$D_a = \gamma_v D_v c_v + \gamma_i D_i c_i. \tag{A.9}$$

In the approximation $\gamma_v \approx \gamma_i \approx 1$ one obtains:

$$D_{\mathrm{a}} \approx D_v c_v + D_i c_i. \tag{A.10}$$

Appendix B

In this Appendix self-consistent consideration of the bulk self-diffusion in the crystal matrix and the two-phase interface kinetics at the bubble surface is presented. For simplicity, only one type of defects is considered (generalization to two types is straightforward following consideration in Section 2).

The vacancy chemical potential $\mu_v(\vec{r})$ in the matrix obeys the Laplace-type equation:

$$\Delta\mu_v = 0. \tag{B.1}$$

Under conditions of thermodynamic equilibrium on the bubble surface, the chemical potential obeys the boundary conditions on this surface:

$$\mu_v^{(\mathrm{eq})} = \mu_{v0} + \gamma_v\omega\sigma_{nn}, \tag{B.2}$$

where σ_{nn} are the normal stresses at the bubble surface ($\vec{n}$ is the normal vector), ω is the atomic volume of uranium atoms, μ_{v0} is the equilibrium vacancy concentration in the absence of stresses, γ_v is the vacancy dilation factor (see Appendix A).

The stresses induced on the bubble surface by an external force $\vec{F}$ exerted on the bubble in the isotropic crystal take the form [10]

$$\sigma_{rr} = -\frac{3F}{4\pi R_{\mathrm{b}}^2}\cos\theta, \quad \sigma_{r\theta} = 0, \quad \sigma_{r\varphi} = 0, (r = R_{\mathrm{b}}), \tag{B.3}$$

where θ is the angle between the vectors $\vec{n}$ and $\vec{F}$.

Solution of Eq. (B.1) with the equilibrium boundary conditions Eq. (B.2) and Eq. (B.3) has the form:

$$\mu_v^{(\mathrm{eq})}(\vec{r}) = \mu_{v0} - \frac{3\gamma_v\omega}{4\pi}\frac{\vec{F}\cdot\vec{r}}{r^3}, \quad (r = R_b). \tag{B.4}$$

In the absence of the thermodynamic equilibrium at the bubble surface when the interface kinetics becomes essential, the boundary conditions on the bubble surface can be searched in the form:

$$\mu_v^{(s)}(\vec{r}) = \mu_{v0} - \alpha\frac{3\gamma_v\omega}{4\pi}\frac{\vec{F}\cdot\vec{r}}{r^3}, \quad (r = R_b), \tag{B.5}$$

where α is an unknown parameter.

In this (non-equilibrium) case the diffusion flux of uranium atoms to the bubble surface is

$$\vec{I}_{\mathrm{dif}} = \frac{\gamma_v D_v c_v}{\omega kT}\vec{\nabla}\mu_v = -\alpha\frac{3D_u}{4\pi kT}\left(\frac{\vec{F}}{R_{\mathrm{b}}^3} - \frac{3\left(\vec{F}\cdot\vec{R}_{\mathrm{b}}\right)\vec{R}_{\mathrm{b}}}{R_{\mathrm{b}}^5}\right), \tag{B.6}$$

whereas the interface kinetic flux is

$$\vec{I}_{\mathrm{int}} = K_1(\mu_v^{(\mathrm{s})} - \mu_v^{(\mathrm{eq})}) = K_1(1-\alpha)\frac{3\omega}{4\pi}\frac{(\vec{F}\cdot\vec{R}_{\mathrm{b}})}{R_{\mathrm{b}}^3}. \tag{B.7}$$

Equating the normal components of the two fluxes $\vec{I}_{\mathrm{dif}}\cdot\vec{n} = \vec{I}_{\mathrm{int}}\cdot\vec{n}$, one obtains:

$$\alpha = \frac{K_1\omega R_{\mathrm{b}}}{K_1\omega R_{\mathrm{b}} + 2(D_{\mathrm{u}}/kT)}. \tag{B.8}$$

The bubble velocity, which obeys the relationship:

$$\vec{v}\cdot\vec{n} = \omega\vec{I}_{\mathrm{dif}}\cdot\vec{n}, \tag{B.9}$$

can be calculated from Eq. (B.9) after substitution of Eq. (B.8) in Eq. (B.6):

$$\vec{v} = \frac{3\vec{F}\omega}{4\pi R_{\mathrm{b}}^3}\frac{K_1\omega R_{\mathrm{b}}\cdot(2D_{\mathrm{u}}/kT)}{K_1\omega R_{\mathrm{b}} + (2D_{\mathrm{u}}/kT)}. \tag{B.10}$$

Therefore, for the bubble mobility that obeys the relationship $\vec{v} = u_b\vec{F}$, one obtains:

$$u_b = \frac{3\omega}{4\pi R_{\mathrm{b}}^3}\frac{K_1\omega R_{\mathrm{b}}\cdot(2D_{\mathrm{u}}/kT)}{K_1\omega R_{\mathrm{b}} + (2D_{\mathrm{u}}/kT)}. \tag{B.11}$$

Finally, for the bubble diffusivity which obeys the Einstein's relationship $D_{\mathrm{b}} = kTu_{\mathrm{b}}$, one obtains:

$$D_{\mathrm{b}}^{(\mathrm{vol})} = \frac{3\omega}{4\pi R_{\mathrm{b}}^3}\frac{K_1\omega R_{\mathrm{b}}\cdot 2D_u}{K_1\omega R_{\mathrm{b}} + (2D_u/kT)}. \tag{B.12}$$

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