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Modelling the variable precipitation of fission products at grain boundaries

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Abstract

We have developed a model for the precipitation of fission products in a grain boundary which embodies a variable reaction rate on the precipitate surface. This enables us to account for modifications of the local fuel chemistry, or to distinguish between the behaviour of different migrating species. In addition, we have assessed the influence of the trapping parameters on the precipitation rate according to different models from the open literature which have been extended in order to incorporate the variable intrinsic reaction rate. The interrelationships among the models have been established while their limitations and range of validity have been discussed. The results reveal that there is a critical value above which the influence of the intrinsic reaction rate, between a fission product and an intergranular trap, on the global precipitation rate becomes negligible.

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1. Introduction

Proper prediction of the fission product behaviour is essential in nuclear fuel performance assessment. On the one hand, the release of fission products, in particular inert gases, not only increases the rod internal pressure and impedes the heat transfer between the fuel pellets and the cladding, it is also crucial in assessing the potential hazard related to the radioactive species. On the other hand, the precipitation of fission products can lead, for instance, to bubble formation, both in the grains and at the grain boundaries. In general, the precipitation at grain boundaries influences the pellet cladding mechanical interaction, the amount of volatile fission products vented during a burst release at high burnup, and it can inhibit the migration of fission products both in the grains and along the grain faces. Accordingly, the correct prediction of intergranular precipitation constitutes an important aspect of a fuel behaviour code.

Trapping or precipitation of fission products can occur at different types of traps such as structural defects, gas-filled bubbles and pores, and metallic precipitates. In addition, volatile fission products such as Cs and I can be immobilised by means of a chemical interaction with the fuel (e.g. uranates) or other fission products (e.g. CsI). As a result, the precipitation or trapping of fission products is dependent on the temperature and burnup [1–6], on the species under consideration [5,7–9], on stoichiometry deviations and additives [10,11], as well as on the geometrical parameters such as the number density and the size of the trapping centres. The influence of these parameters on the precipitation rate is generally embodied in a rate coefficient (k), since the reaction of point defects with traps are usually described in terms of phenomenological rate equations of chemical kinetics. At present, several diffusion-controlled reaction rate coefficients are in use, derived basically from the Smoluchowsky theory of coagulation [12–14]. In these models, the traps are considered to be isolated, that is they are not affected by the presence of each other. The mean field approach [15–17] considers the traps to be isolated particles as well, though in addition it accounts for a source term under

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continuous irradiation conditions. For higher trap concentrations, the diffusion field surrounding a trap will become disturbed by those of neighbouring traps. In order to account for competition between neighbouring traps, Ham [18,19] proposed the cell model without source term and Wood [20] used the modified effective medium approach in two dimensions developed earlier by Brailsford et al. [21,22] in three dimensions. However, the models for the precipitation of volatile fission products, and those who describe void formation by accumulation of vacancies, considered the traps to be perfect absorbers or black spheres. Accordingly, they do not enable us to account for the variable efficiency of the traps at trapping fission products impinging on their surface (k'_{in}) which can result from the variation of the temperature, the stoichiometry, the composition, etc. as indicated above.

The objective of the present paper is two-fold. First, we develop a model for intergranular precipitation of fission products which accounts for the variable trap efficiency, in addition to the overlapping diffusion fields or competition between traps, and the source term under continuous irradiation conditions. The second objective consists in analysing the effect of these parameters on the precipitation rate in grain boundaries according to different theories. To this end, we have extended several models from the open literature in order to account for the variable trapping efficiency of the traps at trapping fission products impinging on their surface. We start by introducing assumptions in order to simplify the mathematical problem at hand. In the following section we present several theories for the rate-theory representation of fission product precipitation in a grain boundary. Subsequently we compare the predictions of the models in steady-state or quasi-steady-state conditions and assess the influence of the various parameters involved. Furthermore we will establish interrelationships among the models and discuss their limitations and range of validity. Although experimental data are not analysed here, an effort has been made to indicate results that should prove useful in this regard.

2. Preliminary assumptions

In our analysis we disregard the creation or nucleation of the traps and, as indicated above, we consider traps in a more general sense. For instance, sinks could correspond to intergranular bubbles and metallic precipitates appearing after a short irradiation time [23–25], as well as defects, e.g. those created by fission fragments. The latter idea is in accordance with the experimental observations on intragranular bubble nucleation in the wake of fission products [26], and with the idea of Khoruzhii et al. [27] about a new retardation force on grain growth in trace irradiated UO_2 due to inclusions in grain boundaries generated when fission tracks intercept the grain face.

The grain boundary traps are assumed to be immobile [28,29], in other words we consider the velocity of the traps to be negligible with respect to the velocity of the fission products. We further adopt a quasi-stationary approach for their growth, that is we presume their size to remain constant during a certain time step.

Each trap is assumed to be circular, corresponding, for example, to the intersection of a lenticular grain boundary bubble with the grain face. We further suppose that all the traps are equi-sized with radius R_{tr} in the plane of the grain boundary, as was indicated for gas-filled bubbles in UO_2 by Tucker [23,30,31].

The fission products arrive at the grain boundary uniformly. A fraction, equal to the fraction of the grain boundary surface occupied by the traps (ϕ), is directly captured by the traps. The other fraction is dissolved in the grain boundary layer and can be trapped when they impinge on a trap while migrating along the grain boundary. Long-range interaction potentials, e.g. appropriate to ionic reactants because of the charge effects, are indirectly accounted for in our investigation by considering a variable effective trapping radius [12,16,17].

Finally, we assume that grain boundary traps exist as separate entities, i.e. they do not interconnect, which implies that ϕ is limited to the order of 40%. Nevertheless, we have extended the calculations for cases where grain faces are almost entirely covered by traps in order to analyse the validity of some approaches.

3. The intrinsic reaction rate at the trap surface

The boundary condition for the fission product concentration at the intergranular trap surface is determined by the intrinsic rate coefficient k_{in}, that is the reaction rate when the migrating species and the traps are in contact. In the event of an infinite intrinsic reaction rate, the absorption of the fission product on collision with a trap occurs instantaneously. Under those circumstances the Smoluchowsky boundary condition (SBC) [15,32,33], sometimes referred to as the black-sphere approximation [12], applies:

$$C_{\mathrm{gb}}(R_{\mathrm{tr}}, t) = 0. \tag{1}$$

In the case of a finite intrinsic reaction rate we obtain the so-called radiation boundary condition (RBC), corresponding to a partial reflection of the particle flux from the reaction surface [12,15,32–34]

$$\oint_{\mathrm{trap}} \vec{J} \cdot \vec{n}\, \mathrm{d}S = 2\pi R_{\mathrm{tr}} D_{\mathrm{gb}} \left.\frac{\partial C_{\mathrm{gb}}(R,t)}{\partial R}\right|_{R_{\mathrm{tr}}} = k_{\mathrm{in}} C_{\mathrm{gb}}(R_{\mathrm{tr}}, t), \tag{2}$$

where k_{in} is the intrinsic rate coefficient on the trap surface and $k'_{in} = k_{in}/2\pi D_{gb}$ is defined as the dimensionless intrinsic rate coefficient. The RBC enables us to assess the influence of the so-called saturation of the intrinsic capture rate on the global capture rate coefficient (k). Such a reduction of k'_{in} could result, for instance, from a lack of vacancies to accommodate the fission gases in a grain boundary bubble or from a temperature variation which in turn can affect the reaction rate of a chemically active fission product with the trap.

Most fission product release models account also for the fact that a fraction of the atoms precipitated or accumulated in the intergranular traps can be re-dissolved into the adjacent grains by interaction with a fission fragment, referred to as irradiation induced re-solution [35–37]. This phenomenon constitutes an essential element in the boundary condition for the transport of the fission products within the grains. However, the irradiation induced re-solution has no direct influence on the reaction rate between the grain boundary traps and the fission products migrating along the grain faces, that is on the boundary conditions on the trap surface. Consequently it will not be considered in the present study.

4. Models for the precipitation rate coefficient

In general, reactions of point defects or fission products with traps are described in terms of chemical rate equations. For this purpose, a rate coefficient (k) is required for each fission product involved. In the following, we will derive a relationship for the capture rate coefficient or the trap strength as a function of the geometrical parameters of the trapping centres, the grain boundary diffusion coefficient of the fission products (D_{gb}) and the efficiency of the traps at trapping fission products impinging on their surface (k'_{in}), according to different approaches.

4.1. The Smoluchowsky approach

For the description of diffusion-controlled reactions, many rate coefficients are derived basically from the Smoluchowsky theory of coagulation in which only one trap species is assumed with such a low concentration that the diffusion field surrounding a trap is not disturbed by the diffusion fields of neighbouring traps [12,14,15,32,33]. This approach is therefore equivalent to the isolated particle approximation mentioned by Ham [18,19] for precipitation of point defects on dislocations.

The Smoluchowsky formalism has been applied successfully to photochemistry [38] and diffusion-influenced fluorescence quenching [15], which is characterised by the kinetic scheme $A^* + B \rightarrow A + B$ where A^* is an excited state of A and B is a quencher acting like an indestructible trap. The model is exact when the diffusion coefficient of A^* approaches zero and the Bs do not interact with each other [15]. Accordingly, this approach is expected to be poor for the problem of absorption of a diffusing particle by static traps, especially at high trap densities where overlapping diffusion fields become important.

Rather than using the concentration of fission products dissolved in the grain boundary, the correlation derived from the Smoluchowsky theory considers the pair-probability function for fission products and traps or the distribution function of the fission products $U(R,t)$ [12,14,15,32]. The distribution function is a solution of the Smoluchowsky equation

$$\frac{\partial U(R,t)}{\partial t} = D_{gb}\,\Delta U(R,t). \tag{3}$$

The partial differential equation is subject to the uniform initial condition $U(R,0) = 1$, and to the SBC or RBC at the reaction surface, while the concentration should remain finite at large distances from the trap. The time-dependent (global) rate coefficient is obtained by integrating the normal component of the flux over the surface of the trap [15,32]

$$k(t) = \oint_{trap} D_{gb}\nabla U\,\mathrm{d}A. \tag{4}$$

Following this procedure, we obtain the time-dependent rate coefficient for intergranular trapping

$$k(t) = \frac{8\left(k'_{in}\right)^2 D_{gb}}{\pi}\int_0^\infty \frac{\mathrm{e}^{-D_{gb}\lambda^2 t}}{F\left(\lambda,k'_{in}\right)}\frac{\mathrm{d}\lambda}{\lambda}, \tag{5}$$

where

$$F\left(\lambda,k'_{in}\right) = \left[\lambda R_{tr}J_1(\lambda R_{tr}) + k'_{in}J_0(\lambda R_{tr})\right]^2 + \left[\lambda R_{tr}Y_1(\lambda R_{tr}) + k'_{in}Y_0(\lambda R_{tr})\right]^2. \tag{6}$$

When the boundary condition at R_{tr} reduces to Eq. (1), this simplifies to the expression obtained by Szabo [15].

4.2. The mean field approach

Alike the previous model, the mean field approach (MFA) corresponds to the isolated particle approximation, subject to the condition that the concentration reaches a constant bulk value at large distances from the trap [15–17]. In the mean field approximation, one assumes that the deviation from the bulk value, $\delta C(R) = C(R) - C_{bulk}$, satisfies

$$D_{gb}\,\Delta\delta C(R) = k_{ss}C_{tr}\,\delta C(R), \tag{7}$$

where C_{tr} represents the number of intergranular traps per unit of grain boundary surface and $k_{ss} = \lim_{t\rightarrow\infty} k(t)$ is the steady-state rate coefficient. This equation is

solved subject to either Eq. (1) or Eq. (2). The steady-state rate coefficient is then equated to the flux at contact, divided by C_{bulk} and multiplied by the trap density C_{tr}. Since $C(R)$ is a function of k_{ss}, this procedure leads to an implicit equation for $k'_{\text{ss}} = k_{\text{ss}}/2\pi D_{\text{gb}}$ which is characteristic for the mean field approximation

$$k'_{\text{ss}} = \frac{k'_{\text{in}}\sqrt{2k'_{\text{ss}}\phi}K_1\left(\sqrt{2k'_{\text{ss}}\phi}\right)}{\sqrt{2k'_{\text{ss}}\phi}K_1\left(\sqrt{2k'_{\text{ss}}\phi}\right) + k'_{\text{in}}K_0\left(\sqrt{2k'_{\text{ss}}\phi}\right)}, \tag{8}$$

where $\phi = C_{\text{tr}}\pi R_{\text{tr}}^2$ represents the fraction of the grain boundary covered by the traps. Taking the limit for $k'_{\text{in}} \to \infty$, corresponding to perfect trap conditions, we obtain the same result as Szabo [15].

The MFA can be shown to be equivalent with the embedding procedure of Brailsford et al. [21,39] which is derived from the rate theory formulation for point defect sink strengths and assumes a steady-state condition as well. In this model, the discrete random array of traps is approximated by an equivalent homogeneous medium. The latter must be such that if we excavate from it a spherical surface of radius R_{SF} and replace it by an equal surface comprised of a spherical shell of a trap free zone surrounding just one inclusion, then the macroscopic properties of the composite thus formed must be the same as those of the medium itself. This is schematically represented in Fig. 1. The trap strength is obtained by solving the following coupled system of differential equations:

$$\begin{aligned} &D\Delta C + S = 0 && R_{\text{tr}} \leqslant R \leqslant R_{\text{SF}}, \\ &D\Delta C + S + S^{\text{e}} - k_{\text{ss}}CC_{\text{tr}} = 0 && R \geqslant R_{\text{SF}} \end{aligned} \tag{9}$$

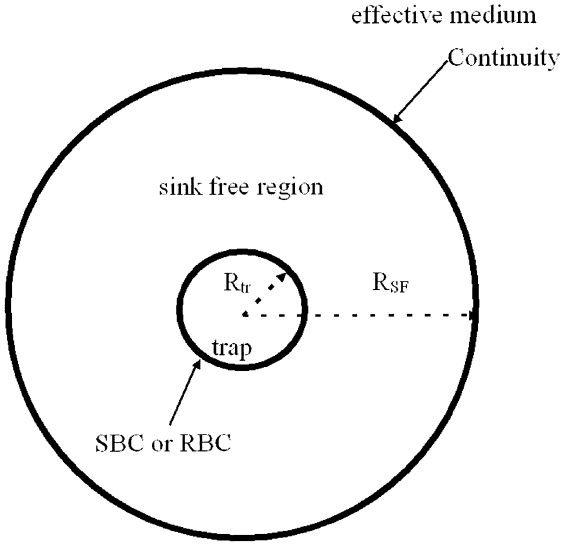

Fig. 1. Schematic representation of the effective medium model.

subject to the boundary condition (1) or (2) on the trap surface, and where S^{e} represents the point defect emission rate from all traps. They derive the net flux of point defects to the central trap and this must equal the net loss rate per sink in the medium. When the trap is directly embedded in the effective medium, in other words, when omitting the trap free region surrounding the trap ($R_{\text{SF}} = R_{\text{tr}}$), the equation governing the fission product concentration in the homogeneous medium becomes equivalent to Eq. (7) since we have $\lim_{R\to\infty} C(R) = C_{\text{bulk}} = (S + S^{\text{e}})/k_{\text{ss}}C_{\text{tr}}$ at large distances from the trap surface.

The embedding procedure is only strictly appropriate when the traps are randomly distributed, although it has been judiciously modified to encompass even regular arrays of traps in a perfect lattice [22]. Wood and coworkers [20,40] have applied this modified effective medium (MEM) approximation to grain boundary bubble swelling. Their model is closely related to the treatment of Speight et al. [41] to void growth on grain boundaries and has been verified by Yang et al. [42] by means of small angle neutron scattering.

Unlike the model derived from the Smoluchowsky theory indicated above, the MFA accounts for a source term under continuous irradiation conditions. Nevertheless, the steady-state rate coefficient obtained with the effective medium procedure can be shown to be equivalent to the quasi-steady-state approximation obtained with modified Smoluchowsky equations [14] in spherical geometry, provided the same boundary conditions are applied at the trap surface. In view of the equivalence of the MFA with the Smoluchowsky approach [15] and with the effective medium approximation mentioned above, we will only present the MFA results. In addition, the rate coefficient derived from the MFA can be expressed as a function of the dimensionless quantities ϕ and k'_{in}.

4.3. The cell model without source term

The cell model is based on the work of Ham [18]. We assume the presence of a regular array of traps with a number density C_{tr}, in accordance with the computations of Tucker for gas-filled bubbles [23,30,31] who indicated that a random array of freshly nucleated bubbles will begin to spread out into a more uniform distribution as they grow. Fixman [43] and Wood [20] have shown that this entails a larger global trapping rate in comparison with an irregular distribution of traps. Given the symmetry of the trap distribution on the grain face, we assume that the same property holds for the concentration profile. A unit cell, or capture surface, surrounding each sphere is then defined as the portion of the surface that can be associated with each circular trap. The entire surface is divided into C_{tr} identical polyhedra or cells each containing one trap at its centre

in order to reproduce (on average basis) the system of surface plus traps. For ease of computation it is convenient to approximate each polyhedron by a circle with a radius chosen to satisfy the requirement that the C_{tr} cells occupy the entire surface. Thus each trap or bubble can be considered to be isolated (Wigner–Seitz approach [44]) in a circular zone of radius R_s defined by $C_{tr}\pi R_s^2 = 1$, or an equivalent rectangular cell with the same size $s^2 = \pi R_s^2$ (cf. Fig. 2). As a result of the symmetry of the concentration profile, the normal component of its gradient vanishes on this surface, or equivalently, an equal number of fission products crosses the cell border in each direction.

We further assume that the concentration satisfies the time-dependent diffusion equation

$$\frac{\partial C_{gb}(R,t)}{\partial t} = D_{gb}\Delta C_{gb}(R,t) \tag{10}$$

at all points of the grain face ($R_{tr} \leqslant R \leqslant R_s$) and we consider a uniform initial distribution of the fission products ($C_{gb}(R, t=0) = \theta$). These circumstances correspond to a post-irradiation annealing situation, where the initial state could result from a very low temperature irradiation such as to immobilise the fission products. The reaction is subsequently resumed at temperatures high enough to allow intergranular diffusion to be operative but low enough so that the fission products in the adjacent grains may be considered to be immobile. This is plausible in the light of the general accepted idea that the activation energy for intragranular diffusion is higher in comparison with the activation energy for intergranular diffusion [45].

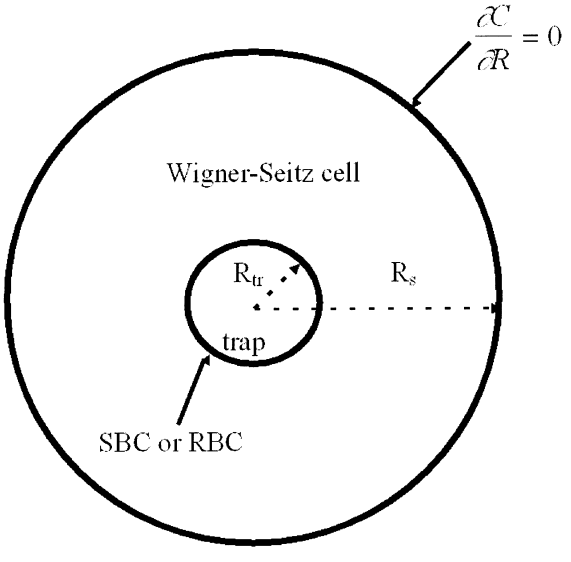

Fig. 2. Schematic representation of the cell model.

The solution to the diffusion equation governing the concentration profile in each cell in case of radiation boundary conditions can be expressed as follows:

$$C_{gb}(R,t) = -\pi k'_{in}\theta \sum_{n=1}^{\infty}\left[\frac{C(\lambda_n, k'_{in}, R)}{F(\lambda_n, k'_{in})}\right] e^{-D_{gb}\lambda_n^2 t}, \tag{11}$$

where

$$C(\lambda_n, k'_{in}, R) = J_0(\lambda_n R)\left[\lambda_n R_{tr} Y_1(\lambda_n R_{tr}) + k'_{in} Y_0(\lambda_n R_{tr})\right] - Y_0(\lambda_n R)\left[\lambda_n R_{tr} J_1(\lambda_n R_{tr}) + k'_{in} J_0(\lambda_n R_{tr})\right], \tag{12}$$

$$F(\lambda_n, k'_{in}) = \left[\frac{\lambda_n R_{tr} J_1(\lambda_n R_{tr}) + k'_{in} J_0(\lambda_n R_{tr})}{J_1(\lambda_n R_s)}\right]^2 - (\lambda_n^2 R_{tr}^2 + k'^2_{in}), \tag{13}$$

where λ_n are the positive roots of

$$\left[\lambda_n R_{tr} J_1(\lambda_n R_{tr}) + k'_{in} J_0(\lambda_n R_{tr})\right] Y_1(\lambda_n R_s) = \left[\lambda_n R_{tr} Y_1(\lambda_n R_{tr}) + k'_{in} Y_0(\lambda_n R_{tr})\right] J_1(\lambda_n R_s). \tag{14}$$

Taking the limit for $k'_{in} \to \infty$, that is when the perfect trap boundary condition applies at R_{tr}, we obtain the same result as obtained by Ham [19].

Integrating the diffusion equation (10) from R_{tr} to R_s and dividing by the surface $\pi(R_s^2 - R_{tr}^2)$ we obtain a balance equation which defines the (global) rate coefficient $k(t)$

$$\frac{d\overline{C}_{gb}}{dt} = -k(t) C_{tr} \overline{C}_{gb}, \tag{15}$$

where

$$\overline{C}_{gb} = \frac{2}{R_s^2 - R_{tr}^2}\int_{R_{tr}}^{R_s} C_{gb}(R,t) R\, dR \tag{16}$$

corresponds to the spatially averaged concentration of the diffusing fission products due to the reaction with the trap species characterised by a number density C_{tr}. Inserting (11) in (16) and deriving with respect to time we obtain the time-dependent rate coefficient

$$k(t) = \frac{D_{gb}}{C_{tr}} \frac{\sum_{n=1}^{\infty}(e^{-D_{gb}\lambda_n^2 t}/F(\lambda_n, k'_{in}))}{\sum_{n=1}^{\infty}(e^{-D_{gb}\lambda_n^2 t}/\lambda_n^2 F(\lambda_n, k'_{in}))}. \tag{17}$$

In the quasi-steady-state, $k(t)$ reduces to a time-independent value (k_{qs}) which is determined by the smallest eigenvalue of (14), also referred to as the first harmonic or fundamental mode

$$\lim_{t\to\infty} k(t) = k_{qs} = \frac{D_{gb}\lambda_0^2}{C_{tr}}. \tag{18}$$

4.4. The cell model with source term

The assumptions are similar to those of the previous model if it is not for the continuous irradiation conditions. This will enable us to assess the effect of a source term on the correction factor to be applied to the rate coefficient, as suggested by Gösele in a three-dimensional spherical geometry [32].

Under continuous irradiation conditions, the right-hand side of the diffusion equation (10) in the cell contains a source term, S, corresponding to the number of fission products arriving at the grain face per unit of surface and time ($\mu m^{-2}\ s^{-1}$). The initial concentration is taken to be zero ($C_{gb}(R, t = 0) = 0$). When the radiation boundary condition applies at the trap surface, the solution to this problem can be written in the form

$$C_{gb}(R,t) = C_{\infty}(R) - \frac{S}{D_{gb}} \times \sum_{n=1}^{\infty} \left[\Psi_n\left(\lambda_n, k'_{in}\right) C\left(\lambda_n, k'_{in}, R\right)\right] e^{-D_{gb}\lambda_n^2 t}, \quad (19)$$

where

$$C_{\infty}(R) = \frac{S}{4D_{gb}}\left[\left(R_{tr}^2 - R^2\right) + R_s^2 \ln\left(\frac{R}{R_{tr}}\right)^2 + \frac{2}{k'_{in}}\left(R_s^2 - R_{tr}^2\right)\right] \quad (20)$$

represents the stationary concentration profile, $C(\lambda_n, k'_{in}, R)$ is given by Eq. (12), λ_n are the positive roots of Eq. (14) and

$$\Psi_n\left(\lambda_n, k'_{in}\right) = \frac{1}{F\left(\lambda_n, k'_{in}\right)}\left\{\frac{R_s\left[\lambda_n R_{tr} Y_1(\lambda_n R_{tr}) + k'_{in} Y_0(\lambda_n R_{tr})\right]}{\lambda_n Y_1(\lambda_n R_s)} - R_s^2 - \frac{k'_{in}}{\lambda_n^2}\right\}, \quad (21)$$

where $F(\lambda_n, k'_{in})$ is given by Eq. (13).

The time-dependent rate coefficient can be inferred from the integrated diffusion equation in a similar way as before

$$\frac{d\overline{C}_{gb}}{dt} = -k(t) C_{tr} \overline{C}_{gb} + S, \quad (22)$$

hence

$$k(t) = \frac{D_{gb}}{C_{tr}}\left[\frac{\left(R_s^2 - R_{tr}^2\right) + 4k'_{in}\sum_{n=1}^{\infty}\Psi_n\left(\lambda_n, k'_{in}\right) e^{-D_{gb}\lambda_n^2 t}}{\frac{D_{gb}}{S}\left(R_s^2 - R_{tr}^2\right)\overline{C}_{\infty} + 4k'_{in}\sum_{n=1}^{\infty}\frac{\Psi_n\left(\lambda_n, k'_{in}\right)}{\lambda_n^2} e^{-D_{gb}\lambda_n^2 t}}\right], \quad (23)$$

where

$$\overline{C}_{\infty} = \frac{S}{8D_{gb}}\left\{\left[\left(R_{tr}^2 - 3R_s^2\right) + \frac{2}{k'_{in}}\left(R_s^2 - R_{tr}^2\right)\right] + \frac{2R_s^4}{\left(R_s^2 - R_{tr}^2\right)} \ln\left(\frac{R_s}{R_{tr}}\right)^2\right\} \quad (24)$$

corresponds to the average concentration in steady-state conditions. The steady-state rate coefficient, denoted by k_{ss}, is obtained from the long-time limit of the time-dependent rate coefficient

$$\lim_{t\to\infty} k(t) = k_{ss} = \frac{S}{C_{tr}\overline{C}_{\infty}} = \frac{8\pi D_{gb}(1-\phi)}{(1-\phi)\left[(\phi - 3) + \frac{2}{k'_{in}}(1-\phi)\right] - 2\ln\phi}. \quad (25)$$

Taking the limit of k_{ss} for $k'_{in} \to \infty$, corresponding to a Smoluchowsky boundary condition at R_{tr}, we obtain the result of the MEM approach [20].

4.5. The model of Kogai

The formulation for grain boundary gas precipitation used by Kogai [13] in his fission gas release model is derived from the Smoluchowsky theory in quasi-steady-state conditions in a spherical three-dimensional geometry (k_{qs}). The corresponding sink strength in the case of a Smoluchowsky boundary condition on the bubble surface can be written as [12,32]

$$k_{qs} = 4\pi R_{tr} D_{gb}. \quad (26)$$

In order to obtain the correct dimensions ($\mu m^2\ s^{-1}$) for the global precipitation coefficient, this rate coefficient has been divided by the distance separating two traps, $s = \sqrt{\pi R_s^2}$. As a result one obtains the following expression for the trapping rate coefficient:

$$k_{qs} = 4\pi D_{gb}\frac{R_{tr}}{s} = 4\sqrt{\pi} D_{gb}\sqrt{\phi}. \quad (27)$$

5. Results and discussion

The comparison of the different models for the (global) capture rate coefficient or the sink strength is performed in terms of the dimensionless rate coefficient $k' = k/2\pi D_{gb}$ in steady-state ($k' = k'_{ss}$) or quasi-steady-state ($k' = k'_{qs}$) conditions. (The results are therefore independent of the grain boundary diffusion coefficient for fission products which is not well characterised at present.) In the event of a regular array of traps with Smoluchowsky boundary conditions, it can be shown

that the second smallest root (λ_1) of Eq. (14) is always larger than $3\lambda_0$ when ϕ ranges between 1% and 99% [46]. Consequently, it suffices to describe the system with a single term in the cell model, except during an initial transient of duration roughly $\tau_0 = 1/D_{gb}\lambda_0^2$. The amount of precipitate associated with the initial transient is only significant when the traps are not small or when the initial distribution is not uniform [18,34]. Whenever the transient is important, the precipitation rate can still be calculated by using the complete analytical solution provided in Sections 4.3 and 4.4 for a regular array of traps, or by neglecting the competition between adjacent traps. In the latter case, the flux is evaluated as if each particle were isolated in an infinite medium. The precipitation rate will be correct for small values of time, when competition is unimportant, though it will be overestimated as the time increases. For large values of the time, when the isolated particle approximation for the precipitation rate exceeds the value given by the (quasi) steady-state solution, the latter forms an excellent approximation.

5.1. The effect of the size and concentration of traps

When the traps operate as perfect absorbers, the dimensionless rate coefficient under steady-state or quasi-steady-state conditions can be expressed as a function of a single parameter, namely the fraction of the grain boundary surface occupied by the traps ($\phi = C_{tr}\pi R_{tr}^2$). The sensitivity of k' to ϕ, computed by means of the models described above, is depicted in Fig. 3. The sink surface fraction ranges from 1% to 99% which covers a wide range of experimental values (in practice ϕ will be limited to the order of 50%). The figure reveals the limited rate coefficient along with a limited variation of k' with ϕ according to the MFA in comparison with the cell models. This reflects the neglect of the overlapping diffusion fields or the competition between traps in the MFA as observed earlier [32] in three dimensions. Similar conclusions hold for the Smoluchowsky theory in the case of trapping of point defects by immobile traps, whereas Szabo [15] indicated that this theory constitutes an exact solution in the quenching problems where traps are mobile and do not interact with one another.

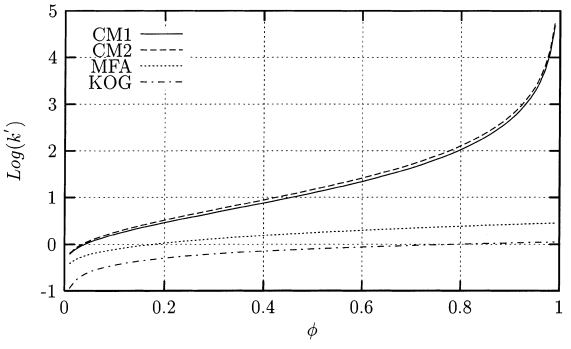

Fig. 3. Dimensionless capture rate coefficient (k') in case of perfectly absorbing traps as a function of the fraction of the grain boundary surface occupied by the traps (ϕ), according to the cell model without source term (CM1), the cell model with source term (CM2), the MFA, the model of Kogai (KOG).

Fig. 3 also features the much lower capture rate coefficient resulting from the expression used in the model of Kogai in comparison with the other models, even for small values of ϕ. The reason for the much lower values is two-fold. The first reason stems from the geometrical effect for the approximation used by Kogai is only valid in three dimensions with spherical traps whereas the other approximations were derived in a two-dimensional geometry. The rate for migrating fission products to be trapped is much larger in the latter case in view of the reduced number of degrees of freedom. Second, the model of Kogai is derived from the Smoluchowsky theory which is equivalent to the isolated particle approximation. As a result, the discrepancy increases as the fraction of the grain boundary surface occupied by the traps is raised. The cell models will tend to ∞ in the limit for $\phi \to 100\%$ unlike the models based on the isolated particle approximation. On the other hand, the results of all the two-dimensional models should be identical for very small values of ϕ, though this is not shown in the plot because of the limited range for ϕ.

5.2. The source term effect

The influence of the continuous irradiation conditions comes also into view in Fig. 3, when comparing the results of the cell models with (CM2) and without source term (CM1). The source term effect can be explained as follows: in the case of annealing conditions, the point defects very close to the trap are captured during an initial transient, that is where not only the lowest eigenfunction in the series solution of the cell model (Eq. (11)) contributes to the precipitation rate. After some time, the precipitation rate will be reduced and only the first harmonic remains in accordance with Eq. (18). However, in the event of continuous irradiation, new point defects will be generated in the vicinity of the trap surface, entailing a faster reaction rate. Nevertheless, the effect of continuous irradiation in two dimensions is much smaller in comparison with the effect of the overlapping diffusion fields, in accordance with observations in three dimensions [32]. In addition, the results of both cell models coincide for small values of the bubble surface fraction ϕ. Consequently, only the results of the cell model including the source term will be presented in the following.

5.3. The effect of the intrinsic reaction rate coefficient

If a reaction barrier at the surface of the traps is taken into account, the dimensionless rate coefficient depends both on the intrinsic reaction rate at the trap surface (k'_{in}) and on the bubble surface fraction (ϕ). According to the model of Kogai, k' is not dependent on k'_{in}, hence his model has not been included in the comparison of the models under radiation boundary conditions. The dimensionless capture rate coefficient, computed by means of the other models, is depicted in Figs. 4 and 5 as a function of ϕ, where the bubble surface fraction ranges from 1% to 99%, for three different values of k'_{in}. The range of k'_{in} from 10^{-3} to 10^{+3} suffices to assess the sensitivity of the dimensionless rate coefficient to this parameter. Indeed, for $k'_{in} = 10^{+3}$, the dimensionless rate coefficient in Figs. 4 and 5 almost converged to the corresponding limiting case of the Smoluchowsky boundary condition in Fig. 3. At decreasing values of the intrinsic rate coefficient, though with $k'_{in} \geqslant 1$, the rate coefficient becomes less sensitive to variations of ϕ according to all the models. The reason for this reduced sensitivity stems from the role played by intergranular traps, decreasing as the intrinsic rate coefficient decreases.

From Figs. 4 and 5 it also comes into view that the capture rate coefficient will be underpredicted by the MFA for large values of ϕ and for all values of k'_{in}, in accordance with the results under perfect trap conditions. This reflects the equivalence with the isolated particle approximation.

The sensitivity of k' to k'_{in} is depicted in Figs. 6 and 7 for three different values of ϕ. It is obvious that a reduction of the intrinsic capture rate coefficient at the trap surfaces will entail a reduction of the global capture rate coefficient. However, from Figs. 6 and 7 there appears to be a critical value for the influence of k'_{in} (namely $k'_{in} \approx 1$) especially for values of $\phi \leqslant 50\%$ which

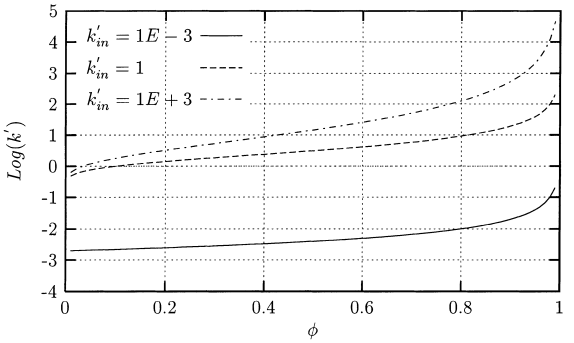

Fig. 4. Dimensionless capture rate coefficient (k') in case of radiation boundary conditions at the trap surface as a function of the fraction of the grain boundary surface occupied by the traps (ϕ), according to the cell model with source term (CM2).

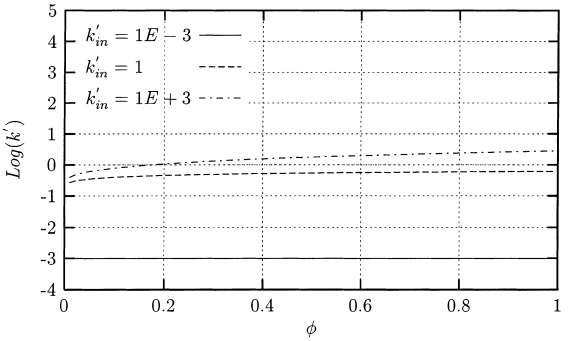

Fig. 5. Dimensionless capture rate coefficient (k') in case of radiation boundary conditions at the trap surface as a function of the fraction of the grain boundary surface occupied by the traps (ϕ), according to the MFA.

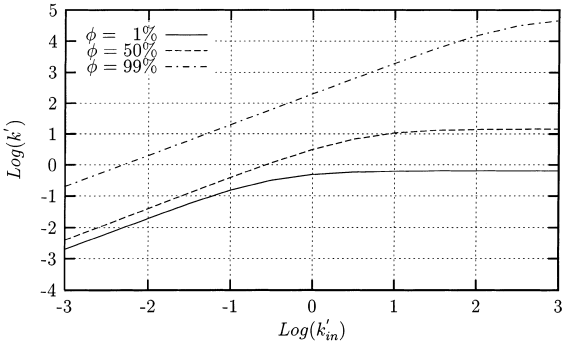

Fig. 6. Dimensionless capture rate coefficient (k') in case of radiation boundary conditions at the trap surface as a function of the dimensionless intrinsic rate coefficient at the trap surface (k'_{in}), according to the cell model with source term (CM2).

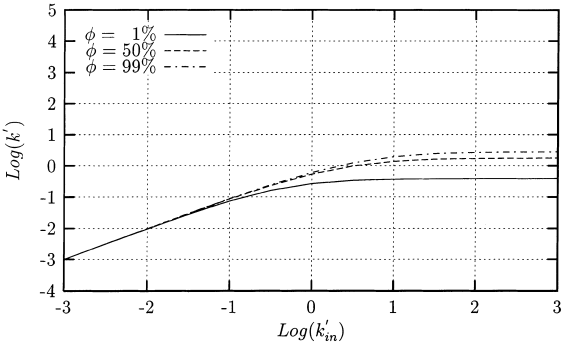

Fig. 7. Dimensionless capture rate coefficient (k') in case of radiation boundary conditions at the trap surface as a function of the dimensionless intrinsic rate coefficient at the trap surface (k'_{in}), according to the MFA.

is of most practical interest. At values of $k'_{in} \leqslant 1$, the influence of k'_{in} on the capture rate coefficient is more pronounced and the sensitivity of k' to ϕ is independent of k'_{in}, entailing parallel curves in Figs. 4 and 5. Physically, this corresponds to the regime where the precipitation of fission products is limited by the intrinsic reaction-rate between the fission product and the precipitate rather than diffusion controlled. This is also reflected in Figs. 6 and 7, where k' becomes proportional to k'_{in}. Such small values of k'_{in} could result for instance from a temperature variation in the case of a chemical active fission product, or from a lack of vacancies in grain boundary bubbles to accommodate fission gases [47,48], or it could be related to thermal re-solution of volatile fission products from gas-filled bubbles [28,49]. Nevertheless, the latter approach is rather controversial [50,51] since it conflicts with the long-held assumption that volatile fission products, in particular inert gases, are essentially insoluble in UO_2.

For values of $k'_{in} \geqslant 1$, the relative change of the rate coefficient is almost independent of the relative change of the intrinsic capture rate coefficient (cf. Figs. 4–7) except when $\phi \geqslant 50\%$. In present day models for fission gas release [13,28,52], the intrinsic reaction rate coefficient for intergranular bubbles is taken to be infinite, that is they consider Smoluchowsky boundary conditions. In practice, the intrinsic rate coefficient for different fission products and intergranular traps is unknown. However, it seems reasonable to assume that $k'_{in} > 1$ for several fission products (e.g. noble gases, metallic fission products), given the negligible solubility and the observation of metallic precipitates associated with gas-filled bubbles at grain boundaries [23–25]. Accordingly, it seems well justified to apply the Smoluchowsky boundary conditions, for instance in the model of Matthews and Wood [40] under stationary conditions for inert gases. In addition, the relative insensitivity of k' to k'_{in} for $k'_{in} \geqslant 1$ could explain the similar global precipitation rate at grain boundaries of several fission products. For instance, Walker et al. [6] found that similar amounts of Xe and Cs were precipitated in the grain boundary gas bubbles of UO_2 fuel above 1573 K, although dissimilarities would be expected from the differences in charge, ionic radius and solubility.

6. Summary and conclusions

We have developed a model for precipitation of fission products in a grain boundary which embodies the variable efficiency of the traps at trapping fission products impinging on their surface, in addition to the overlapping diffusion fields between traps and the source term under continuous irradiation conditions. The variable intrinsic reaction rate enables us to account for modifications of the local fuel chemistry or to distinguish between the behaviour of different migrating species.

The effect of the various parameters, especially k'_{in}, on the intergranular precipitation rate has been assessed according to different approaches. Results in steady-state or quasi-steady-state conditions reveal that models derived from the Smoluchowsky theory of coagulation, the MFA and the effective medium approximation are only accurate when the trap concentration is very low since they neglect the competition between neighbouring traps. The formalism adopted by Kogai in a fission gas release model is based on the Smoluchowsky theory in a three-dimensional spherical geometry and underpredicts the capture rate by one order of magnitude. In addition, it does not enable one to account for variations of the intrinsic reaction rate. The cell model including a source term appears to provide an appropriate expression for the capture rate coefficient, for it embodies all the variable parameters indicated above and it can be applied to non-stationary conditions as well.

There appears to be a critical value for the influence of k'_{in} (namely $k'_{in} \approx 1$) on k', especially for values of $\phi \leqslant 50\%$ which is of most practical interest. At values for k'_{in} in excess of 1, which is believed to be representative for inert gases, the influence of k'_{in} on the precipitation rate coefficient k' is reduced significantly. This is beneficial given the uncertainty pertaining to this parameter. In addition, it justifies the assumption of an infinite intrinsic reaction rate coefficient for intergranular bubbles in fission gas release models and it could explain the similar behaviour of different species for which $k'_{in} > 1$. Nevertheless, experimental work is required in order to acquire quantitative information about k_{in}.

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