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Models of Grain Boundary Bubbles Behaviour in UO_2-Fuel during Rapid Heatup

Vladimir Likhanskii and Leonid Matweev

Troitsk Institute for Innovation and Fusion Research - TRINITI, Russia

ABSTRACT: The models have been developed which describe the behaviour of nonequilibrium grain boundary bubbles in spent nuclear fuel under the conditions of rapid heatup without irradiation. Two relaxation mechanisms of the excessive bubble pressure have been investigated: the cracking of the matrix along grain boundaries (the "brittle" mode of relaxation), the growth of bubble volume due to vacancy flows ("diffusion" mode of relaxation). The cracking criterion is obtained and the eventual crack sizes are calculated. In the case when cracking does not occur, dynamics of overpressurised bubbles is described which is determined by diffusion flows of vacancy and interstitials.

1 INTRODUCTION

It is common knowledge that the nuclear fuel properties essentially changes during its irradiation. This is mainly connected with the accumulation of the gaseous fission products (GFP) in the form of solid solution and bubbles and with the microstructure changes of the fuel - the evolution of dislocation structure, cracking. An information about these properties is especially important for the simulation of reactivity initiated accidents when an essential GFP release occurs under the conditions of relatively low energy deposition (far from fuel melting).

For example in experiment [1], about 20% of accumulated GFP were released during a very short period of *10-100 ms* from the fuel with burnup of approximately *40 MWd/kgU* at the energy deposition of *100 Cal/g*. Such rapid release of GFP at sufficiently low temperature was associated with the mechanism of grain boundary microcracking in [2], [3]. An essential part of FGP accumulates in the bubbles on the grain boundaries during fuel irradiation. The strength of interatomic bonds in the grain boundaries is lower than that in the volume. The fuel pellet heatup leads to the growth of the bubble pressure which in turn may provoke the cracking of the pellet along grain boundaries (the "brittle" mode of relaxation) and to a fast FGP release. When the temperature increases slowly, the pressure in the bubbles may relax due to the vacancy income to the bubbles ("diffusion" mode of relaxation). In this case the critical pressure will not be reached and cracking will not occur. In the work [2] the criterion of the change-over from the "brittle" relaxation mode to the "diffusion" one has been obtained. However authors of [2] did not take into account some factors. These are the decrease of average vacancy concentration in the grain boundary region due to their absorption by the bubble, the lenticular form of grain boundary bubble, which leads to the stress concentration near its tip. The decrease of vacancy concentration may lead to an essential suppression of the "diffusion" growth of the bubble and as a result to the change in the conditions of the development of the "brittle" mode of relaxation

In the present paper the model has been developed, which describes the both relaxation modes of grain boundary bubbles during rapid heatup of uranium dioxide fuel. The cracking conditions have been determined and formulas for the eventual crack sizes have been derived depending on the pressure increase in the bubbles and on stresses in the pellet. An expression for the diffusion growth rate of the grain boundary bubbles has been derived, which takes into account different sources of point defects generation and annihilation.

2 THE MICROCRACKING PROCESSES

The considerable mechanical stresses can occur in a fuel pellet under the conditions of rapid heatup. Firstly, the pressure increase in the bubbles leads to the growth of the stresses in their vicinity. Secondly, the nonuniform heatup of the pellet is the source of mechanical stresses.

The grain boundary bubble is characterised by the radius in the boundary plane R, by the amount of gas atoms in it N and by the angle θ at the tip (Fig.1). For grain boundary bubble in UO_2 $\theta \approx 50^0$. According to [4] the bubbles in the fuel with the burnup of 3÷4.5% are strongly overpressurised: the pressure in the bubbles of the radii $10 \div 100$ nm is equal approximately to 1 GPa. This value significantly exceeds the equilibrium pressure which is determined by surface tension (approximately 0.2 GPa for $R \approx 10$ nm). The increase of the pressure with heatup is defined by the equation of state for *Xe*.

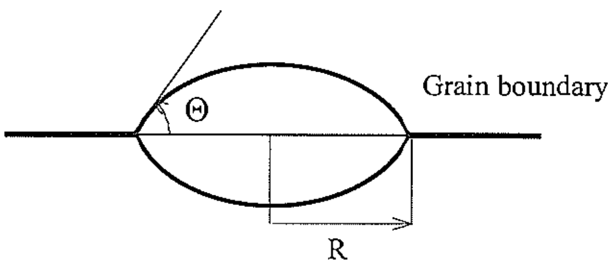

Fig.1 The grain boundary bubble.

The change in the radial temperature distribution leads to the appearance of mechanical stresses which can be calculated from the solution of thermoelastic problem [5]. In the case when the temperature fall takes place in the narrow outer layer the hoop stresses in this layer can reach the value of ~ 1 GPa for $\Delta T \approx 300K$. Thus for determination of microcracking criterion (the condition of the cracking along grain boundaries) it is necessary to take into account two factors: the increase of the pressure inside the bubbles and thermoelastic stresses.

The stresses around the grain boundary bubble can be calculated under the following simplifications. We shall consider the bubble stretched in one direction along grain boundary, that is in two dimension case. The bubble is supposed to have an elliptical shape with the relation of half-axes equal to: $a_1/a_2 = \sin\theta/(1-\cos\theta)$. According to [6], the maximum tensile stresses appear near the boundary of the bubble on the prolongation of the greater axis. Tensile stresses $(\sigma_{yy})_{max}$ are approximately equal to $3.5\cdot\delta P$ if the stresses far from the bubble are zero. Here δP is the excessive gas pressure in the bubble. The value of $(\sigma_{yy})_{max}$ is slightly conservative since the acute angle at the tip of the grain boundary bubble is an additional stress concentrator. When the tensile stresses at the tip of the bubble exceed some critical value: $(\sigma_{yy})_{max}>\sigma_{crit}$, the cracking begins. σ_{crit} depends on the grain boundary properties. One can suppose that the strength of the grain boundary is lower than the theoretical limit $\sigma^0_{crit}\approx\mu/2\pi\approx 12\ GPa$ [7] approximately by the factor of 1.5÷2. For $\sigma_{crit}\sim 0.5\cdot\sigma^0_{crit}$ the cracking criterion is fulfilled at $T/T_0\approx 1.7$. It should be emphasised that here the "microscopic" strength of interatomic bonds is considered but not the "macroscopic" one which for polycrystallised uranium dioxide is equal approximately to $150\ MPa$ [8]. It should be also noted that in the present paper the effect of bubble interaction is not taken into account.

The analogous calculations can be made for the stresses at the tip of elliptical bubble when the temperature gradient changes. The tensile stresses at the tip are equal to $\sigma_{max}\approx 5.2\cdot\sigma_{\theta\theta}$ for the bubbles stretched along the pellet radius near the pellet edge ($\sigma_{rr}\approx 0$) [6]. The estimation shows the stresses $\sigma_{crit}\sim 0.5\cdot\sigma^0_{crit}$ can be reached at the temperature fall of $\Delta T\approx 300\text{-}400\ K$. Once the stresses in the pellet are caused by the excessive pressure in the bubbles and by the temperature gradients simultaneously, the sum of the both stress sources will present in the cracking criterion. For example, for grain boundary bubbles stretched along radius near the edge of the pellet the criterion takes the form:

$$3.5\delta P + 5.2\sigma_{\theta\theta} > \sigma_{crit}.$$

For the constant inner pressure the tensile stresses at the tip of the crack grow $\propto\sqrt{L}$ [7], where L is the crack length. During cracking the volume increases and the pressure falls. This may lead to the crack stabilisation. The displacement of the surfaces of the round crack $Y(r)$ in the direction perpendicular to its plane is described by the formula $Y(r)=\pm[2(P+\sigma)/\pi\mu]\sqrt{L^2-r^2}$ (r is the distance from the crack centre) [9] and its volume is equal to $V=4(P+\sigma)L^3/3\mu$. Taking into account the initial volume of the bubble $V_0=\chi R_0^3$, where $\chi=2\pi\left(2-3\cos\theta+\cos^3\theta\right)/\left(3\sin^3\theta\right)\approx 2$ for $\theta=50^0$, the estimation of the ultimate volume of the crack takes the form:

$$V\approx V_0+4(P+\sigma)L^3/3\mu\ , \tag{1}$$

where P is the final pressure. The crack growth breaks off when the stress intensity factor $K=2(P+\sigma)\sqrt{L/\pi}$ decreases up to critical value $K_{crit}\approx\sqrt{\mu\left(2\gamma_S-\gamma_{gb}\right)}$ [7,9]. The critical value of stress intensity factor is determined by the state of grain boundaries and can depend on the fuel burnup and on the temperature. For fresh fuel $K_{crit}\sim 2\cdot 10^5\ Pa\cdot m^{1/2}$. The ultimate crack length can be calculated from the system of equations: gas pressure P, tensile stress σ and crack length L are connected by the expression $(P+\sigma)=K_{crit}\sqrt{\pi/4L}$, L determines the volume of the crack according to Eq. (1), and the equation of state for Xe is given by Van der Waals' formula. Ultimately for the value $X=(L/R_0)^{0.5}$ the following equation is valid:

$$\left(\frac{K_{crit}\sqrt{\pi/4R_0}}{\mu}-\frac{\sigma}{\mu}X\right)\left[1+\frac{4}{3\chi}\frac{K_{crit}\sqrt{\pi/4R_0}}{\mu}\left(1+\frac{BP_0}{kT_0}\right)X^5\right]=\frac{P_0}{\mu}\frac{T}{T_0}X\ , \qquad (2)$$

where $B=85\AA^3$ is the parameter of nonidiality of Xe, k is Boltzmann constant. From Eq.(2) it follows that crack length increases with the temperature jump T/T_0 and initial bubble radius R_0. When the fuel is heated from $T_0=600K$ up to $T=1500K$ and in the case when tensile stresses are absent the solution of Eq.(2) for $R_0=10nm$ gives $L/R_0\approx 2$ and for $R_0=15nm$ $L/R_0\approx 2.9$. The grain boundary surface occupied by the crack increases approximately by 4 and 8.4 times respectively in comparison with the surface occupied initially by the bubble. The process of crack growth for $K>K_{crit}$ is very fast as the crack tip moves approximately with the sound velocity.

3 THE "DIFFUSION" RELAXATION MODE OF OVERPRESSURISED GRAIN BOUNDARY BUBBLES

The pressure in the bubble, on being heated, is determined by the temperature and its volume. The pressure necessary for cracking may not be achieved if the rate of the volume growth due to the diffusion mass transfer is sufficiently high. Let us consider the mechanism of diffusion growth of the bubbles due to the vacancy accumulation. It is usually supposed (see [2]) that the grain boundary region is the main source of the vacancies. For the growth of bubble volume the following expression has been obtained in [2]:

$$dV/dt = 4\pi D_b hR\delta P\omega/lkT, \qquad (3)$$

where h is the grain boundary width, ω is the atomic volume, R is the bubble size, l is the bubble spacing in the grain boundary, D_b is the grain boundary diffusion coefficient of uranium in UO_2. For the value $D_b h$ the dependence $D_b h = 6.31\cdot 10^{-9}\exp(-35340/T)$ is used [2]. The expression (3) is valid if either only small part of the amount of vacancies in the grain boundary is absorbed by the bubble during bubble growth, or the sources exist which maintain the equilibrium vacancy concentration (for example, free surfaces or pores without gas). If the bubbles are strongly overpressurised ($\delta P\omega/kT>>1$) or they cover a significant part of the grain boundary surface then their growth rate can be sufficiently decreased due to the vacancy depletion. In this situation the limited rate of the vacancy generation and their interaction with interstitials must be taken into account.

Let us consider the case when there are no sources in grain boundary region assotiated with free surfaces and irradiation. The vacancy concentration is determined by the thermal generation according to the Frenkel mechanism, annihilation with the interstitials, diffusion to the bubbles and exchange of vacancies between the grain boundary and the bulk of the grain:

$$\frac{\partial C_v}{\partial t}-D_{vb}\frac{1}{r}\frac{\partial}{\partial r}r\frac{\partial C_v}{\partial r}=q-\alpha C_v C_i+\frac{2J_v}{h}\ . \qquad (4)$$

On the bubble surface the vacancy concentration depends on the bubble pressure $C_v(R) = C_{v0} exp(-\delta P\omega/kT)$. At $r=l$ from the symmetry it follows: $\partial C_v/\partial r|_l = 0$. The flux J_v takes into account the exchange of vacancies between the grain boundary and the bulk of the grain. For vacancy concentration in the grain volume the following equation is used:

$$\partial C_{vg}/\partial t = D_{vg}\, \partial^2 C_{vg}/\partial y^2 + \beta\left(C_{vg0} - C_{vg}\right). \tag{5}$$

Here C_{vg0} is the equilibrium vacancy concentration in the bulk, $\beta\left(C_{vg0} - C_{vg}\right)$ describes vacancy source determined by the dislocations with the density ξ, $\beta \approx D_{vg}\xi$. Axis y is directed inside the grain. C_v and C_{vg} at $y=0$ are connected by the relation $C_{vg}\big|_{y=0} \approx C_v \exp(-\Delta\varepsilon/kT)$, where $\Delta\varepsilon$ is the difference between the formation energies in these regions. The equations analogous to Eq.(4) and Eq.(5) describe the concentration of uranium interstitials C_i and C_{ig}. The solution of this system of equations under the conditions of given temperature regime determines the vacancy flux to the bubble and, hence, the growth rate of its volume. We will derive approximate expression for bubble growth rate basing on simplified analysis of the proceeding processes.

Two characteristic times determine the dynamics of the vacancies in the grain boundary region: the diffusion time $\tau_1 \approx 4l^2/\pi^2 D_{vb}$, and the time of vacancies - interstitials annihilation $\tau_2 \approx (\alpha C_i)^{-1}$. Here $\alpha \approx 4\pi b(D_{vb}+D_{ib})$, b is the interatomic distance. When the interstitial concentration in the grain boundary region is less than $C_i^* \sim 1/\left(10l^2 b\right)$ (for this $\tau_1<\tau_2$) the vacancies generating on the area of $S=\pi(l^2-R^2)$ flow to the bubble and the interstitial store. Once C_i achieves C^*_i the annihilation of the vacancies with interstitials becomes the main process. After the time $\tau_3 \approx C_i^*/q$ the amount of vacancies forming in the grain boundary region and absorbed by the bubble decreases and growth of the bubble becomes slower. The change of the bubble volume is negligible in the time τ_3: $\delta V/V_0 \sim hb^2/R_0^3$

Since the concentration of point defects in the grain boundary region is not equilibrium, the exchange of point defects takes place between the boundary and the bulk of the grain. The vacancies flow from the grain bulk to the grain surface is estimated from Eq.(5) and from the connection of C_v and C_{vg} providing $exp(\delta P\omega/kT)>>1$: $\delta N_v \approx 2S\, D_v\, C_{vgo}\, \sqrt{\xi}\, t$. The transition time to the steady-state solution at constant temperature is $\tau_4 \approx (D_{vg}\xi)^{-1}$. The same expressions are obtained for interstitials where one must substitute D_v for D_i and C_{vg0} for $C_{ig0} \cdot C_i^*/C_{i0}$. The resultant flux of the vacancies to the bubble includes two parts: the vacancies that come from the bulk and the noncompensated vacancies formed as the result of leaving of interstitials from grain boundary. The expression for the growth rate of the bubble takes the form:

$$dV/dt = 2S\left(D_v C_{vg0} + D_i C_{ig0}\, C_i^*/C_{i0}\right)\sqrt{\xi}\,. \tag{6}$$

The increase of the bubble volume during the time τ_3 is negligible. Eq.(6) takes into account two ways of the vacancies delivery to the bubble. The first one is determined by the vacancy flow from the bulk of the grain. The second one is due to generation of the vacancies and interstitials in the grain boundary region, the departure of the interstitials to the bulk and their subsequent annihilation on sinks. The values of the parameters in Eq.(6) are presented in the literature with significant scattering. Thus it is impossible to determine the dominate process. For $C_i^*/C_{i0}=1$ the factor in the brackets in Eq.(6) is the self-diffusion coefficient of uranium, and for estimation of the growth rate of the bubble volume we may write:

$$dV/dt \approx 2S\,D_{ug}\sqrt{\xi}\,. \tag{7}$$

Here D_{ug} is the self-diffusion coefficient of uranium in the grain bulk for which the following expression is adduced in the literature: $D_{ug}\approx 1.09\cdot exp(-51980/T)$ $см^2/c$ [10,11]. From Eq.(7) one can estimate the time τ required to increase the bubble volume up to $\delta V\approx 0.7V_0$. Such volume increase provides the bubble pressure decrease to the level of $\delta P\omega/kT<1$. At $T=1500K$, $dV/dt\approx 5\cdot 10^{-22} sm^3/s$ one obtains $\tau\approx 100s$; at $T=1650K$, $dV/dt\approx 10^{-19} cm^3/s$, $\tau\approx 5s$; at $T=1950K$, $dV/dt\approx 1.2\cdot 10^{-17} cm^3/s$, $\tau\approx 0.04s$. In the experiments [1] and [3] the time of heatup was of the order of ten milliseconds. From the estimations cited above it follows that in these experiments the "brittle" mode of relaxation developed that led to a rapid fission product release from the grain boundaries of the fuel pellet. When the rate of heatup is fixed then the rate of the bubble growth is to be calculated with the regard to temperature dependencies.

The times of relaxation calculated according to Eq.(3) appear to be much smaller than that obtained above and the conditions of microcracking in the model [2] are not achieved. It should be emphasised that in accordance with Eq.(3) the growth rate of the bubble volume increases with the decrease of the distance l between the bubbles. This dependence is not physically true because with the decrease of l the amount of vacancies generating per one bubble decreases as it follows from Eqs.(6), (7).

The vacancy diffusion coefficient in the grain boundary is very high. The vacancies which generate at the free surfaces by a Shottky mechanism could quickly penetrate into the inner regions of the pellet and lead to relaxation of the grain boundary bubbles. For $D_{vb}\approx 10^{-5} cm^2/s$ an estimation of vacancy penetration depth $L\approx\sqrt{D_{vb}t}$ gives $0.1mm$ for $10s$. However, these vacancies will be extensively absorbed by overpressurised bubbles and their penetration inside the pellet will be significantly suppressed.

When the vacancies penetrate deep into the pellet their concentration is described by the diffusion equation with sinks. The strength of the sinks is defined by the concentration of the grain boundary bubbles and their overpressurisation. The relaxation zone consists of three regions. Near free surface the bubbles relaxed and the strength of vacancy sinks reduces to zero. Far from free surface the bubbles are overpressurised, the strength of the sinks is high and vacancy concentration decreases exponentially. In intermediate region the bubble growth takes place and the strength of the sinks decreases gradually. This region moves deep into with the velocity dL/dt where L is the size of the outer region. In the quasistationary approximation the vacancy flux from the free surface can be estimated as $J_1\approx D_{vb}\left(C_v(T)-C_1\right)/L$, where $C_v(T)$ and C_1 are the vacancy concentrations on the free surface and on the boundary between the first and the second regions. If one consider this flux to be equal to the amount of vacancies absorbed by the bubbles in a unit time $dL/dt\cdot(Vn)/(\omega h)$ then the expression for the size L takes the form

$$L \approx \sqrt{D_{vb}t} \cdot \sqrt{\frac{2hC_v(T)\omega}{nV}}.$$

Here n is the concentration of overpressurised bubbles over the unit area of the grain boundary, V is the ultimate volume of the bubbles determined by the equilibrium condition $NkT/V \approx 2\gamma_s \sin\theta / R$. We suppose $C_i \approx 0$ for estimation of the maximum velocity of vacancy penetration front. For the values of the parameters $n/h \approx 1.5 \cdot 10^{16} cm^{-3}$, $R_0 \approx 10nm$, $C_{v0}(T)\omega \approx 10^{-6}$, $T \approx 1500K$ the following estimation of the penetration depth of the "relaxation front" is obtained $L \approx 5 \cdot 10^{-3} \sqrt{D_{vb}t}$. Thus the absorption of the vacancies by overpressurised bubbles impedes to their "fast" penetration deep into the pellet.

4 CONCLUSION

The models of grain boundary porosity relaxation have been developed for rapid out-of-pile heatup of the UO_2 fuel. Under the conditions of temperature increase high local stresses occur in the spent fuel related both to the increase of inner bubble pressure and to the nonuniformity of heatup. Simultaneously the diffusion processes accelerate. The relaxation of the nonequilibrity can take place due to the cracking of the pellet along grain boundaries (the "brittle" mode of relaxation) or due to the growth of the bubble volume owing to the diffusion mass transfer: the income of the vacancies and leaving of the interstitials. The type of the developed mode essentially influences the ultimate state of the fuel and depends both on the initial conditions and on the rate of the heatup.

The following results have been obtained:

1. The criterion of the development of the "brittle" relaxation mode has been derived. The criterion relates the level of fuel heatup, the bubble parameters and the properties of crystalline matrix when the stresses in the matrix are determined by the pressure inside the bubbles and by the nonuniformity of fuel pellet heatup.
2. The process of the bubble relaxation has been investigated and the expression for the ultimate crack size has been derived.
3. The expression for relaxation rate of the grain boundary bubbles has been obtained at various temperatures, concentration of the bubbles, their overpressurisation and the strength of volume sources of point defects.

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