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Kinetics of UO_2 oxidation in steam atmosphere

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Abstract

An adsorption model for calculation of UO_2 oxidation in H_2O/H_2 gas mixture is proposed. The model is based on the assumption that the rate of fuel oxidation by steam is controlled mainly by surface oxygen exchange reactions which are described in terms of Langmuir-like theory. Corrections to the oxidation rate related to the volume diffusion of oxygen are taken into account using an adiabatic approach to the diffusion problem. Parameters of the model were optimized on the experiments with steam pressure up to 10^5 Pa at 1200 to 2000 K. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Nuclear fuel oxidation is an important phenomenon affecting fission product behaviour. As indicated by a number of studies, uranium dioxide shows a very wide range of non-stoichiometric states: the O/U ratio can vary from 1.65 to 2.25, but substoichiometric UO_{2-x} exists only at high temperatures. Fuel oxidation in steam produces a hyperstoichiometric composition changing the transport properties in the fuel. In particular, variation of stoichiometry changes diffusion coefficients for oxygen and noble gases in the lattice, substantially affecting the release of fission products.

The behaviour of uranium dioxide in a steam–hydrogen mixture has been examined in a number of studies. All the studies on self-diffusion in UO_2 showed that the anionic mobility exceeds that of the cationic by many orders of magnitude. Therefore, changes in fuel stoichiometry occur via oxygen migration in solid fuel [1].

In early works of fuel oxidation kinetics, the rate of fuel oxidation was assumed to be limited by the rate of oxygen diffusion in the UO_{2+x} lattice [2]. Carter and Lay [3] showed directly that the surface oxygen exchange is a relatively slow process. Their experiments were conducted with the samples of 1.5×10^{-3} to 5×10^{-3} m thick in CO_2/CO atmosphere at 1000 to 1700 K. Evidence of significant stoichiometry gradients within the UO_{2+x} samples was not found for both oxidation and reduction processes. The oxidation rates were found to be inverse proportional to the sample thickness and increasing with the CO_2 partial pressure. Carter and Lay concluded that in the case of thin samples not the solid-state diffusion, but the interaction at the gas–solid interface is the rate-limiting step of fuel oxidation. The oxygen diffusion in the solid may be a rate limiting process for large size pellets.

In this paper we concentrate on the models of surface oxygen exchange kinetics. We analyze briefly the existing models employed for simulation of UO_2 oxidation and propose an adsorption model of oxidation kinetics. The parameters of the model are optimized using experimental data, and then the results of simulations of the experiments not used for the parameter optimization are presented. Finally, oxidation of thick samples is discussed and a modification of the model equations is considered, which then takes into account the effect of oxygen volume diffusion dealt with in the context of adiabatic approximation.

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2. Models of oxidation kinetics

To describe the fuel oxidation kinetics, a general form of the rate equation can be used,

$$\rho_U V \frac{\mathrm{d}x}{\mathrm{d}t} = SK(x,T) f(P_{H_2O}, P_{H_2}) \left(1 - \frac{q(x)}{q_0}\right), \qquad (1)$$

where x is the stoichiometry deviation averaged over the sample volume, ρ_U is the uranium molar density, V and S are the volume and surface area of specimen, respectively. The left hand side of this equation is the derivative of the number of oxygen moles in the solid fuel. In general, the right hand side representing the difference between adsorption and desorption flows should be a function of x_b that is the stoichiometry deviation in the boundary layer. However, we consider here the case of sufficiently thin fuel samples when the difference between x and x_b can be neglected. Corrections related to this difference are considered in Section 6 of the paper.

The reaction rate constant $K(x,T)$ is a function of temperature and may depend on the stoichiometry deviation. The function f is included into the kinetic equation to take into account the effect of gas pressure on the oxidation rate.

The right hand side of Eq. (1) includes the driving force of equilibration that should be proportional to the difference between the oxygen activities in the gas phase and at the fuel surface. The oxygen activity in the gas phase is represented here by the steam-to-hydrogen pressure ratio, $q_0 = P_{H_2O}/P_{H_2}$ (throughout this paper the values of pressures in equations are divided by 10^5 Pa and given in dimensionless quantities; the values of temperature T are given in K). Since the components of the gas phase are assumed to be in chemical equilibrium with respect to each other, q_0 is determined by the mass action equation $P_{H_2O}/P_{H_2} = K_{H_2O}\sqrt{P_{O_2}}$ with $K_{H_2O} = \exp(30\,165/T - 6.95)$. The function $q(x)$ specifies the steam-to-hydrogen pressure ratio of such a gas mixture that is in equilibrium with the given stoichiometry deviation x. This function can be represented as $q(x) = K_{H_2O}\sqrt{\overline{P_{O_2}}(x)}$, where $\overline{P_{O_2}}(x)$ is the equilibrium oxygen pressure over solid UO_{2+x} defined, for instance, by Blackburn [4] or Lindemer and Besmann [5] correlations.

It is worth pointing out that the steam and hydrogen partial pressures included in Eq. (1) characterize the gas phase state in the vicinity of the solid surface. In general, the oxygen absorption by solid fuel accompanied by hydrogen generation can affect the gas phase composition near the surface which depends also on the gas flow rates and the gas phase diffusion. To separate the problem of fuel oxidation from that of the mass transfer in the gas phase, we suppose here that the gas phase composition is controlled by experimental conditions independent of the oxidation rate.

2.1. Carter–Lay model

The simplest model of oxidation kinetics in CO_2/CO mixture was proposed by Carter and Lay [3] and was applied later to the case of steam–hydrogen atmospheres by Cox et al. [6].

On the basis of existing experimental data, Carter and Lay supposed that the function $q(x)$ depends linearly on the stoichiometry deviation. Then $q(x)/q_0 = x/x_{eq}$ where x_{eq} is the equilibrium stoichiometry deviation determined by the oxygen pressure in the gas phase. The rate constant was assumed to be independent of x. Then, the kinetic equation can be represented in the following form:

$$\dot{x}(t) = (S/V)\,\alpha(t)\,(P_{H_2O})^m\,(x_{eq} - x(t)). \qquad (2)$$

The surface exchange coefficient α was measured by Cox et al. [6,7] and Lewis et al. [8] for the case of oxidation in pure steam at $P_{tot} = 10^5$ Pa in the temperature range 1073–1873 K. They found that $\alpha = 0.365 \exp(-23\,500/T)$ (in m/s). Similar results were obtained by Abrefah et al. [9].

In the original Carter–Lay model, the exponent m was assumed to be unity because the adsorption flow was suggested to be proportional to the steam partial pressure. Later, in the set of experiments on oxidation in steam–argon atmosphere with the partial pressure of H_2O varying from 0.25×10^5 Pa to 10^5 Pa [9], it was shown that the oxidation rate increases approximately as square root of the steam pressure, that is $m = 0.5$.

It should be noted that, as a rule, when the Carter–Lay model is applied, an additional parameter is used to fit the calculated stoichiometry deviation to experimental data [10,11]. This parameter is the area-to-volume ratio, which can differ from the simple geometrical ratio due to surface imperfections. Unfortunately, there are no reliable methods for checking the effective area of oxidation, and therefore, there is a substantial uncertainty in the value of this parameter. The effective area may exceed the geometrical one by a factor of up to four.

2.2. Gala–Grabke model

The other model of UO_2 oxidation was considered by Abrefah et al. [9]. This model is based on the approach developed by Gala and Grabke [12] to describe iron oxidation in steam–hydrogen atmospheres. Following Ref. [12], Abrefah et al. assumed that the reaction of steam with the solid fuel surface goes through two elementary steps: dissociation at the surface with adsorption of hydroxyl radical, and subsequent surface decomposition of hydroxyl resulting in formation of adsorbed oxygen, which then migrates into the solid.

$$\begin{aligned} H_2O(g) &\rightleftarrows OH(ads) + H(ads) \\ OH(ads) &\rightleftarrows O(ads) + H(ads). \end{aligned} \tag{3}$$

Hydrogen adsorption and desorption, $2H(ads) \rightleftarrows H_2(g)$, were assumed to be quite rapid compared to reactions (3), so that the gas–solid interface is in equilibrium with respect to hydrogen exchange.

With these assumptions, the oxidation rate is determined by the slowest reaction. In the kinetic Eq. (1), this idea is represented by the form of the pressure dependence of the oxidation rate. If the reaction of steam dissociation is the rate-limiting step, then this dependence is the same as in the original Carter–Lay model: $f(P_{H_2O}, P_{H_2}) = P_{H_2O}$. Alternatively, when the rate-controlling step is the reaction of hydroxyl decomposition, then the pressure dependence factor takes the form: $f(P_{H_2O}, P_{H_2}) = P_{H_2O}/\sqrt{P_{H_2}}$. Additionally, in this model it is assumed that the reaction rate constant depends on the stoichiometry deviation as $K(x,T) = k_1(T) q(x)^{-n}$. Here, the positive exponent n is an adjustable parameter of the model.

Using the Gala–Grabke model, the large set of experiments was analyzed in Ref. [9] to find optimum values of the parameters $k_1(T)$ and n for each experiment. Unfortunately, there is a significant scatter in the values obtained [9]. This is mostly true for the exponent n, which is recognized by the model as a 'universal' constant, independent on the external conditions and the sample geometry. However, comparison with the experimental data does not agree with this assumption. For instance, in the set of similar experiments with polycrystalline UO_2 samples in pure steam atmosphere at $T = 1623$ K the value of n varied from 0.01 to 0.37.

3. Adsorption model of fuel oxidation

In order to specify the pressure dependence of the oxidation rate as controlled by surface exchange reactions, the oxidation kinetics can be described using Langmuir adsorption theory. According to Langmuir theory [13], adsorption is concentrated around certain centers that correspond to energy minimums. Both the number of these centers, N_s, and their arrangement at the surface depend on specific properties of the solid.

Let us consider, for simplicity, fuel oxidation in pure steam. Besides H_2O, this atmosphere includes H_2, O_2, OH molecules, atomic H and O. Let n_{H_2O}, n_O and n_i be the numbers of moles of adsorbed water, oxygen and other gas components, respectively. Even at high temperatures ranging from 1000 to 2000 K, concentrations of dissociation products are lower than the steam concentration by several orders of magnitude. Therefore, it is quite reasonable to assume that $n_i \ll n_{H_2O}$, and to consider only the water adsorption at the fuel surface ignoring the contribution of other gases to adsorption,

$$H_2O(g) \underset{k_a}{\overset{\nu_w}{\rightleftarrows}} H_2O(ads). \tag{4}$$

Oxygen appears in the solid, as assumed, due to surface decomposition of water molecules:

$$H_2O(ads) \underset{\nu_h}{\overset{k'_a}{\rightleftarrows}} O(ads) + H_2(g). \tag{5}$$

Following Carter–Lay and Gala–Grabke, the gas–solid interface is assumed to be in equilibrium with respect to hydrogen exchange. Adsorption rates can be represented in the form

$$\frac{d}{dt}\bar{n}_O = J^+_O - J^-_O, \qquad \frac{d}{dt}n_{H_2O} = J^+_{H_2O} - J^-_{H_2O}, \tag{6}$$

where J^+ and J^- are the ingoing and removal fluxes, $\bar{n}_O$ designates total moles of oxygen in the solid fuel including adsorbed moles. The oxidation rate is related to $\dot{\bar{n}}_O$ by the equation $\dot{\bar{n}}_O = V\rho_U dx/dt$.

According to Eqs. (4) and (5), the adsorption and removal fluxes of water molecules are given by

$$\begin{aligned} &J^+_{H_2O} = SWj_{H_2O}\left(n_s - N_O - n_{H_2O}\right)/n_s + Sj_{H_2}\kappa n_O/n_s, \\ &J^-_{H_2O} = (k_a + k'_a)n_{H_2O}. \end{aligned} \tag{7}$$

Here, $j_{H_2O} \sim P_{H_2O}/\sqrt{RTM_{H_2O}}$ and j_{H_2} are the incident current density of water vapor and hydrogen considered as ideal gases, W is the adhesion probability of H_2O molecules, κ is the constant of the inverse reaction (5), $n_s = N_s/N_A$ and N_A is Avogadro's number, k_a and k'_a are the rate constants for desorption and surface decomposition of H_2O molecules, respectively. The oxygen fluxes can be represented as $J^+_O = k'_a n_{H_2O}$, $J^-_O = Sj_{H_2}\kappa n_O/n_s$. Substituting the fluxes into Eq. (6) yields

$$\begin{aligned} \dot{n}_{H_2O}/n_s = {}& \nu_w\left(1 - \theta_{H_2O} - \theta_O\right) + \nu_h\theta_O \\ & - (k_a + k'_a)\theta_{H_2O}, \end{aligned} \tag{8}$$

$$\dot{\bar{n}}_O/n_s = k'_a\theta_{H_2O} - \nu_H\theta_O. \tag{9}$$

Here, $\theta_{H_2O} = n_{H_2O}/n_s$ and $\theta_O = n_O/n_s$ are the fractions of adsorption centers occupied by water molecules and oxygen atoms, respectively. The frequencies ν_i are defined by $\nu_w = SWj_{H_2O}/n_s$ and $\nu_h = S\kappa j_{H_2}/n_s$.

Evaluations of the frequencies ν_w and ν_h at $P = 10^5$ Pa in the temperature range 1500–1700 K yield $\nu_w \sim 10^9$–10^{10} s^{-1}, $\nu_h \sim 10^5$–10^6 s^{-1}. We assume that the rate constant of the surface decomposition, k'_a, can be estimated by the rates of the fuel oxidation process. Then, $k'_a \sim 10^3$ s^{-1}, and with the surface decomposition of water molecules, it can be considered as the rate-controlling reaction, $k'_a \ll \nu_w$, ν_h. This means that in the oxidation time scale, defined by $\tau_{ox} \sim (k'_a)^{-1}$, the number of adsorbed water molecules is a slowly varying function of time that satisfies a quasi-steady-state limit of Eq. (8). On the other hand, it is assumed that the oxygen diffusion in solid UO_{2+x} is a rapid process. Then the fraction of the adsorption centers occupied by oxygen is a function of the stoichiometry deviation and the steam pressure that can be defined from Eq. (9) at the stationary conditions for a given stoichiometry deviation x. Thus, Eqs. (8) and (9) can be reduced to the following rate equation:

$$\frac{dx}{dt} = k^*(T, P_{H_2O})\left(\frac{S}{V\rho_U}\right)\left(1 - \frac{q(x)}{q_0}\right), \tag{10}$$

where the effective rate constant is defined by $k^*(T, P_{H_2O}) = k(T) f(P_{H_2O})$, and the pressure dependence of the oxidation rate is described by a Langmuir-type function,

$$f(P) = \frac{A(T)P}{1 + A(T)P}. \tag{11}$$

Both constants, k and A, depend on temperature only and can be expressed in terms of the surface decomposition rate constant and the adsorption rate constant.

4. Fitting and validation

Determination of the coefficients of the adsorption model was performed using the results obtained by Abrefah et al. [9]. In their experiments, samples of unirradiated polycrystalline UO_2 were oxidized in H_2O–H_2–Ar mixtures at a total pressure of 10^5 Pa. The experiments were subdivided into three series with the following conditions: (1) pure steam, temperature ranging from 1273 to 1623 K; (2) steam–hydrogen mixtures with the initial hydrogen content varied from 0.09 to 0.5% by volume in the temperature interval 1473–1623 K; (3) steam–argon mixtures with the steam partial pressure varied from 10^5 Pa to 0.25×10^5 Pa at 1623 K.

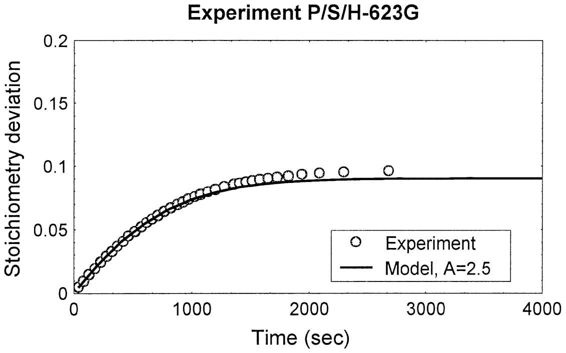

Fig. 2. Stoichiometry deviation in steam–H_2 mixture, P/S/H-623G [9] (full pressure is 10^5 Pa, steam pressure is 10^5 Pa).

Using the fitting procedure, we considered the first two experimental series to determine the effective rate constant at $P_{H_2O} = 10^5$ Pa. The results of calculations can be approximated by the Arrhenius-type function

$$k^*(T,1) = 10^4 \exp(-21\,253/T - 2.43) \times (\mathrm{mol/m^2\,s}) \tag{12}$$

with a relative root-mean-square deviation less than 20%. Processing of the data of the third experimental series (H_2O–Ar mixtures with $P_{tot} = 10^5$ Pa and $P_{H_2O} = 10^5$ Pa, 0.5×10^5 Pa, 0.33×10^5 Pa, 0.25×10^5 Pa) enables us to estimate the constant $A(T)$ at $T = 1623$ K as $2 \le A(T) \le 2.5$. It should be pointed out that with this value of A, the function $k^*(T,P)$ at $T = 1623$ K in the interval $0.2 \le P \le 1.0$ practically coincides with $\sqrt{P}$. This is in a good agreement with the findings in Ref. [9]. Additionally, we considered the oxidation experiment performed by Lewis et al. [11] with steam–He mixture at $T = 1473$ K and $P_{H_2O} = 0.03 \times 10^5$ Pa. Estimation of $A(T)$ for this temperature gave $2.5 \le A(1473) \le 3$. Since there are no

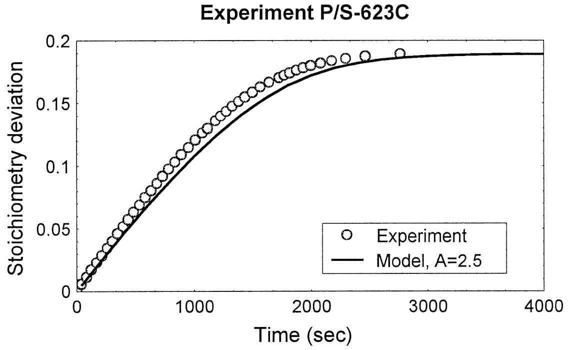

Fig. 1. Stoichiometry deviation in steam, P/S-623C [9] (full pressure is 10^5 Pa, steam pressure is 0.9961×10^5 Pa).

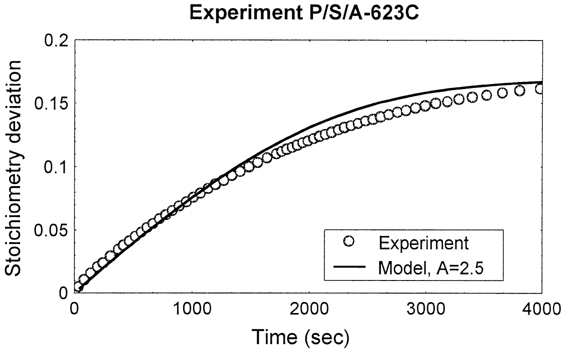

Fig. 3. Stoichiometry deviation in steam–Ar mixture, P/S/A-623C [9] (full pressure is 10^5 Pa, steam pressure is 0.33×10^5 Pa).

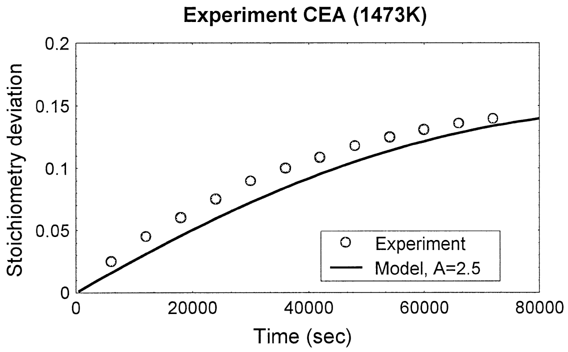

Fig. 4. Stoichiometry deviation in low pressure steam–He mixture [11] (full pressure is 10^5 Pa, steam pressure is 0.33×10^5 Pa).

other data on fuel oxidation kinetics at different temperatures and steam pressures, we used A as a constant value of temperature. The best fitting of experimental results are achieved at $A\cong2.5$.

The obtained rate constant was substituted into Eq. (10) to calculate the oxidation kinetics for all the experiments reported in Ref. [9]. In Figs. 1–3 the model predictions are compared with the data of three typical experiments: with steam, 99.7% H_2O–0.3% H_2 and 33% H_2O–67% Ar mixtures at $T=1623$ K.

Additionally, we considered the oxidation experiment performed by CEA [11] with steam–helium mixture at 1474 K and low steam pressure, $P_{H_2O}=0.03\times10^5$ Pa (Fig. 4). The results for uranium dioxide were applied for simulation of experiments with reactor UO_2 fuel. We considered three experiments performed by Lewis et al. [11] for fuel samples with burn up 19.5 MW d/kg U. As it is seen from the plots in Figs. 5–7, the results of simulations are in good agreement with the experimental data.

5. Diffusion corrections to the oxidation models

The models discussed above describe the oxidation kinetics in the case of thin fuel samples for which the

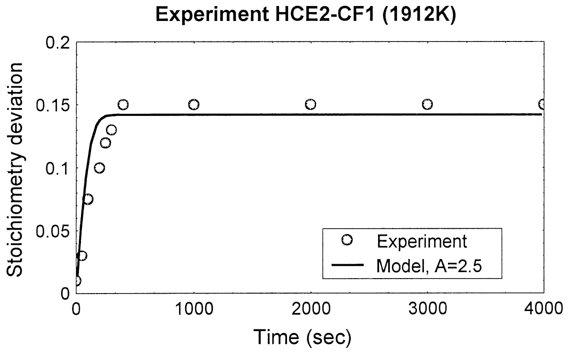

Fig. 5. Stoichiometry deviation in steam–Ar mixture, HCE2-CF1 [11] (burn up 19.5 MW d/kg U, steam pressure is 0.889×10^5 Pa).

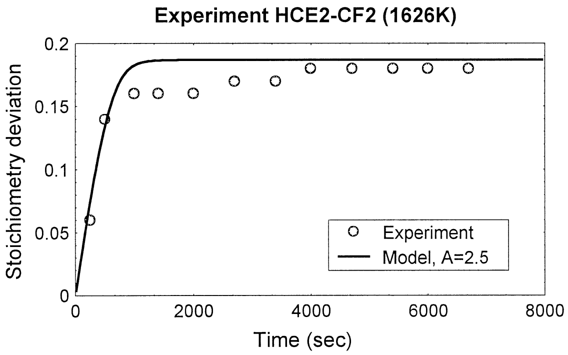

Fig. 6. Stoichiometry deviation in steam–Ar mixture, HCE2-CF2 [11] (burn up 19.5 MW d/kg U, full pressure is 10^5 Pa, steam pressure is 0.889×10^5 Pa).

difference between the average and boundary values of stoichiometry deviation, that is $\bar{x}(t)$ and $x_b(t)$, can be neglected (in Sections 1–4, the average stoichiometry deviation has been denoted by $x(t)$). Such samples were used in the experiments [9,11].

For real fuel pellets, the rate of diffusion process may be compared with the surface exchange rate at high temperatures. In the temperature range from 1000 to 1500 K at stoichiometry deviation of $x>0.01$, the oxygen self-diffusion coefficient in fuel matrix is of the order of 10^{-11}–10^{-10} m^2/s [14,15], while the chemical diffusion coefficient is of the order of 10^{-9} m^2/s at $T\sim1300$ K [1]. On the other hand, according to Refs. [3,6,7], the surface exchange coefficient increases from about 10^{-9} to 10^{-7} m/s with temperature increasing from 1200 to 1600 K. Comparison of the characteristic diffusion and oxidation times shows that the oxidation process is controlled by the reactions at the gas–solid interface for relatively thin samples with thicknesses less than 3×10^{-3} m.

In a general case, the process of UO_2 oxidation includes oxygen migration within the fuel governed by the

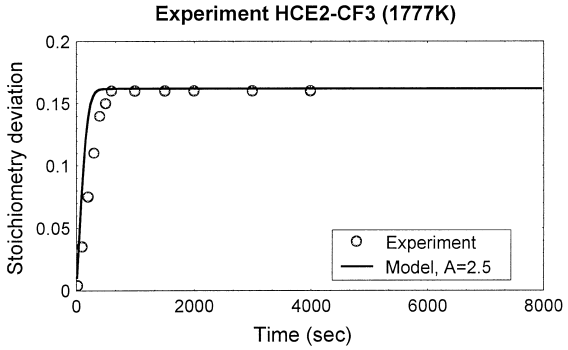

Fig. 7. Stoichiometry deviation in steam–Ar mixture, HCE2-CF3 [11] (burn up 19.5 MW d/kg U, full pressure is 10^5 Pa, steam pressure is 0.889×10^5 Pa).

diffusion equation for the local stoichiometry deviation $x(r,t)$,

$$\frac{\partial}{\partial t} x(r,t) = D\Delta x(r,t),$$

$$D\nabla x(r,t)|_{r=r_\mathrm{b}} = \alpha^* F(x(r_\mathrm{b},t)), \tag{13}$$

where D is the solid state diffusion coefficient of oxygen, r_b defines the position of the sample boundary. The boundary condition for the volume diffusion of oxygen is determined by the surface oxidation rate given by Eq. (10). Namely, in Eq. (13), α^* is related to the rate constant of the adsorption model by $\alpha^* = k^*(T,P_{\mathrm{H_2O}})/(x_\mathrm{eq}\rho_\mathrm{U})$, while the function $F(x)$ is defined as

$$F(x) = x_\mathrm{eq}(1 - q(x)/q_0). \tag{14}$$

In the case of the Carter–Lay approximation, when $q(x)/q_0 \approx x/x_\mathrm{eq}$, the diffusion equation can be solved explicitly for geometries of planar layer, cylinder, rectangular parallelepiped and sphere. In the analysis of the problem (Eq. (13)), Eq. (14) shows that for samples of intermediate sizes close to that of real $\mathrm{UO_2}$ pellets the zero-dimensional kinetic Eq. (10) can be simply modified to account for the diffusion effects within a sufficient accuracy.

Let us consider in some detail the case of infinite planar layer of the thickness h. According to Eqs. (13) and (14), the average stoichiometry deviation satisfies the following equation:

$$\tau_\mathrm{ox}\dot{\bar{x}}(t) = F(x_\mathrm{b}(t)), \qquad \tau_\mathrm{ox} = h/2\alpha^*. \tag{15}$$

In order to specify a relation between $\bar{x}(t)$ and $x_\mathrm{b}(t)$ we suppose, at first, the boundary oxygen flux to be a constant F in time interval $\Delta t = t - t_0$. In this case, the exact solution of the diffusion problem can be represented as

$$x(z,t) = \frac{F\alpha^*}{hD}(2D\Delta t + z^2) + x_D(z,t), \tag{16}$$

where the function $x_D(z,t)$ includes the contributions of the higher eigenmodes of the diffusion problem. These contributions decrease with increasing time at least as $\exp(-t/\tau_\mathrm{dif})$ where the characteristic diffusion time is $\tau_\mathrm{dif} \approx h^2/(4\pi^2 D)$. Therefore, at time intervals $\Delta t > \tau_\mathrm{dif}$, the average and boundary oxygen concentrations are related by $x_\mathrm{b}(t) \approx \bar{x}(t) + hF\alpha^*/6D$.

In the case of real boundary flux $F(x)$, we introduced the parameter $\beta = |F'(x)| \cdot \tau_\mathrm{dif}/\tau_\mathrm{ox}$ with $F' = \mathrm{d}F/\mathrm{d}x$ and assume that $\beta \ll 1$. This means that the boundary flux is a slowly varying function of time in the time scale determined by τ_dif, that is $F(x_\mathrm{b}) \gg \tau_\mathrm{dif}\dot{x}_\mathrm{b}(t)|F'(x_\mathrm{b})|$. Then, the lowest approximation in the adiabatic parameter β yields

$$x_\mathrm{b}(t) = \bar{x}(t) + \xi F(x_\mathrm{b}(t)), \qquad \xi = h\alpha^*/6D. \tag{17}$$

Thus, addition of Eq. (17) to Eq. (15) closes the problem.

Eqs. (15) and (17) can be also applied to other 1D problems with the appropriate definition of the parameters: $\tau_\mathrm{ox} = R/2\alpha^*$ and $\xi = R\alpha^*/4D$ for an infinite cylinder of the radius R, $\tau_\mathrm{ox} = R/3\alpha^*$ and $\xi = R\alpha^*/5D$ for a sphere of the radius R.

Note that in 1D problems, the accuracy of the adiabatic approach decreases with increasing value of the dimensionless parameter ξ. Comparison of numerical solution of the exact diffusion problem for $\bar{x}(t)$ in the time interval up to $\bar{x}(t) = 0.9\ x_\mathrm{eq}$ with that of the adiabatic approximation shows that the relative root-mean-square deviation between the solutions is less than 5% for $\xi \leq 1$.

The similar approach can be applied to the 2D problem of a finite cylinder with the radius R and the length h. In this case, the boundary values of stoichiometry deviation depend on coordinates as $x_{\mathrm{b}z}(r,t) = x(z = \pm h/2, r, t)$ and $x_{\mathrm{b}r}(z,t) = x(z, r = R, t)$. Therefore, as it follows from Eq. (13), the average stoichiometry deviation satisfies the equation

$$\tau_\mathrm{ox}\dot{\bar{x}}(t) = F(\bar{x}_{\mathrm{b}z}(t)) + \frac{h}{R}F(\bar{x}_{\mathrm{b}r}(t)), \tag{18}$$

where $\tau_\mathrm{ox} = h/2\alpha^*$. The functions $\overline{F}$ are defined as

$$\overline{F(x_{\mathrm{b}z}(t))} = \frac{2}{R^2}\int_0^R F(x_{\mathrm{b}z}(r,t))\, r\,\mathrm{d}r,$$

$$\overline{F(x_{br}(t))} = \frac{2}{h}\int_0^{h/2} F(x_{\mathrm{b}r}(z,t))\,\mathrm{d}z. \tag{19}$$

To construct an adiabatic solution for this problem, we again start with an exact solution of the diffusion equation for the case of constant boundary fluxes given by

$$x(z,r,t) = \frac{\alpha^*}{2RD}\left(2sF_z z^2 + F_r r^2 + 2D(sF_z + F_r)\Delta t\right) + x_D(z,t). \tag{20}$$

The diffusion time is defined here as $\tau_\mathrm{dif}^{-1} \approx D(4\pi^2/h^2 + \mu_1^2/R^2)$, where $\mu_1 \approx 3.8$ is the first extreme of Bessel function $J_0(\mu)$. For $\Delta t \gg \tau_\mathrm{dif}$, Eq. (20) leads to the approximate relationships for the average volume stoichiometry and average boundary ones. As in the 1D problem, we assume that the real boundary flux is a slowly varying function of time in the diffusion time scale. Then the lowest approximation in the adiabatic parameter yields

$$\bar{x}_{\mathrm{b}z}(t) = \bar{x}(t) + \frac{h\alpha^*}{6D}F(\bar{x}_{\mathrm{b}z}(t)),$$

$$\bar{x}_{\mathrm{b}r}(t) = \bar{x}(t) + \frac{R\alpha^*}{4D}F(\bar{x}_{\mathrm{b}r}(t)). \tag{21}$$

Finally, we suppose that

$$\overline{F(x_{\mathrm{b}z}(t))} \cong F(\overline{x_{\mathrm{b}z}}(t)), \quad \overline{F(x_{\mathrm{b}r}(t))} \cong F(\overline{x_{\mathrm{b}r}}(t)). \tag{22}$$

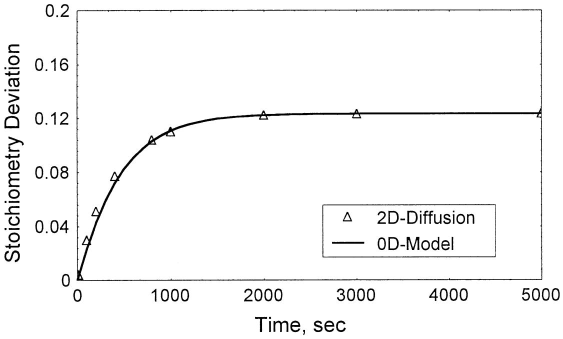

Fig. 8. Oxidation kinetics for cylindrical UO_2 pellet: $R = 5 \times 10^{-3}$ m; $h = 1.5 \times 10^{-2}$ m; $T = 2073$ K; $D = 10^{-8}$ m^2/s.

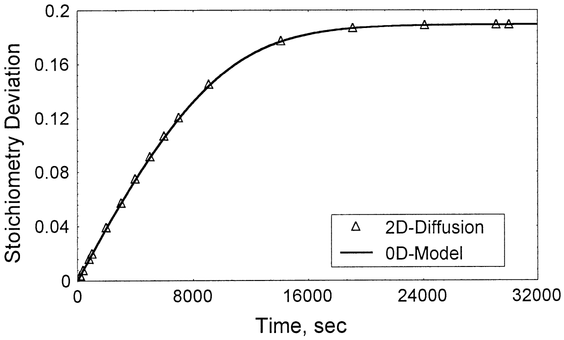

Fig. 9. Oxidation kinetics for cylindrical UO_2 pellet: $R = 5 \times 10^{-3}$ m; $h = 5.0 \times 10^{-2}$ m; $T = 1623$ K; $D = 5 \times 10^{-9}$ m^2/s.

Substituting Eq. (22) into Eqs. (18) and (21) leads to a closed set of equations for the average stoichiometric deviation.

To check the efficiency of the adiabatic (0-D) approach, we used an exact solution of the fuel oxidation problem based on the model of surface oxidation chemistry (Eq. (10)) coupled with 2D numerical module for modeling of oxygen diffusion. Calculations were carried out for a cylindrical sample with the diameter of 10^{-2} m. The results compared in Figs. 8 and 9 are in a good agreement with each other. However, as expected, the computational cost was sufficiently low for 0-D model.

6. Conclusion

In the present work, the adsorption model of UO_2 oxidation in H_2O/H_2 gas environment is developed. The results obtained with this model are in a good agreement with available experimental data. The model is valid for following values of parameters.

In the approximate temperature interval 1200–2000 K. The lower temperature limitation is due to the possible region where the phase transition from UO_{2+x} to U_3O_8 can essentially affect the oxidation process. Full description of the fuel behaviour in steam above 1900–2000 K should also include accounting for the process of fuel evaporation.

In steam, pressure ranges from 0.03×10^5 Pa to 10^5 Pa. These restrictions are related, first of all, to the limited conditions covered by experimental data. Pressure dependence of the fuel rate oxidation is sufficiently different in adsorption model, in Carter–Lay and in Gala–Grabke models at high steam pressures. To expand the range of validity of the fuel oxidation model, it is necessary to perform additional experiments on fuel oxidation at high pressure in a wide temperature interval.

It should also be noted that simulations of the experiments with the considered models were performed under the assumption that there are no differences between the gas phase composition near and far from the solid surface. Estimates show that in the conditions of the considered experiments, determined by the experimental geometry and gas flow rates, these differences affect the oxidation rate insignificantly. In the case of more general conditions, description of the oxidation process should include self-consistent consideration of the gas phase mass transfer.

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