Journal of Nuclear Materials 383 (2009) 201–208

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Growth of the interaction layer around fuel particles in dispersion fuel

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ARTICLE INFO

Article history:
Received 23 June 2008
Accepted 31 July 2008

ABSTRACT

Corrosion of uranium particles in dispersion fuel by the aluminum matrix produces interaction layers (an intermetallic-compound corrosion product) around the shrinking fuel spheres. The rate of this process was modeled as series resistances due to Al diffusion through the interaction layer and reaction of aluminum with uranium in the fuel particle to produce UAl_x. The overall kinetics are governed by the relative rates of these two steps, the slowest of which is reaction at the interface between Al in the interaction layer and U in the fuel particle. The substantial volume change as uranium is transferred from the fuel to the interaction layer was accounted for. The model was compared to literature data on in-reactor growth of the interaction layer and the Al/U gradient in this layer, the latter measured in ex-reactor experiments. The rate constant of the Al–U interface reaction and the diffusivity of Al in the interaction layer were obtained from this fitting procedure. The second feature of the corrosion process is the transfer of fission products from the fuel particle to the interaction layer due to the reaction. It is commonly assumed that the observed swelling of irradiated fuel elements of this type is due to release of fission gas in the interaction layer to form large bubbles. This hypothesis was tested by using the model to compute the quantity of fission gas available from this source and comparing the pressure of the resulting gas with the observed swelling of fuel plates. It was determined that the gas pressure so generated is too small to account for the observed delamination of the fuel.

1. Introduction

For five decades, so-called dispersion fuel has powered many test and research reactors worldwide. The current version consists of U or U, Mo spheres initially 50–75 μm diameter dispersed in a matrix of aluminum (recently with added Si) in the form of a plate ~0.4 mm thick. This fuel 'meat' is clad on both sides with plates of aluminum to form a fuel element.

The formation of an undesirable 'interaction layer' around the fuel sphere has been the subject of many studies (see Refs. [1,2] and the references therein). Fig. 1 shows the geometry of the process, which is basically corrosion of metallic uranium by metallic aluminum. The interaction layer (designated as IL) that has developed around the fuel spheres is an intermetallic compound UAl_x where x is between 3 and 4. There has been some question as to whether the IL is crystalline or amorphous, but recent work has confirmed the latter, at least under irradiation [3]. A consequence of amorphization of the IL may be its inability to retain fission gas.

At high burnup, swelling of the fuel element (also called 'blistering' or 'pillowing') is observed. Metallography of the cross section shows a split of the fuel meat along its midplane. It is generally believed that this phenomenon is due to fission gas released from the interaction layer. The fission gas produced in the fuel particle (hereafter designated as FP) forms tiny bubbles in the grain boundaries [2]. Fission gas, along with the other fission products, is transferred to the IL as the U–Al reaction consumes the fuel particle.

Previous theoretical analyses of growth of the IL [1,4] were based upon the suppositions that:

(i) both uranium and aluminum are mobile species in the IL; (ii) the kinetics are controlled by counter-diffusion of these two species. Rate-limiting reaction kinetics at the interfaces of the IL with the fuel sphere (labeled A) and the IL with the matrix (labeled B) were not considered, nor was transfer of fission products to the IL along with uranium.

The objective of the present work is twofold: (i) to model the growth of the IL; (ii) to determine the quantity of fission gas in the IL, which, if released, could cause separation of the fuel meat by overpressurization. For simplicity, the dispersed phase is pure uranium (in place of U–Mo) and the matrix is pure aluminum (instead of Al–Si).

For the purpose of this analysis, the fission process is described by

U-235 → fission-product pairs

and

U-235 → U-236

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doi:10.1016/j.jnucmat.2008.07.035

Nomenclature

Symbol	Meaning	value
Subscripts		
A	at interface A	
B	at interface B	
Al	aluminum	
eq	equilibrium	
FP	fuel particle	
fpp	fission-product pair	
IL	interaction layer	
U	uranium	
0	initial value	
Nuclear quantities		
e	U-235 enrichment	0.2
σ_{abs}	U-235 thermal-neutron absorption cross section	99 b
σ_{fiss}	U-235 thermal-neutron absorption cross section	582 b
σ_{tot}	U-235 total thermal-neutron cross section	681 b
γ	$\sigma_{abs}/\sigma_{tot}$	0.15
φ	thermal neutron flux	$cm^{-3}\ s^{-1}$
F	fission-rate density $cm^{-3}\ s^{-1}$	
bu	fraction of U-235 consumed	
E	fraction of U consumed	P_{fpp}/P_{U0}
Molar volumes		
υ_{fpp}	fission-product pairs in FP	
υ_U	uranium in FP	12.5 cm^3/mol
β	$\upsilon_{fpp}/\upsilon_U$	see Section 5
υ'_{fpp}	fission-product pairs in IL	
υ'_U	uranium in IL	see H
H	υ'_U/υ_U	3.8
β'	$\upsilon'_{fpp}/\upsilon'_U$ see Section 5	
Moles		
P_{fpp}	total moles fpp in IL + FP	
P_U	total moles U in IL + FP	
P_{U0}	initial moles U	$P_U + P_{fpp}$
N_U	moles U in FP	
N_{fpp}	moles fpp in FP	
N'_U	moles U in IL	
N'_{fpp}	moles fpp in IL	
f	fraction of total U in FP	N_U/P_U
f	fraction of total fpp in FP	N_{fpp}/P_{fpp}
Volumes		
V_{FP}	of FP	
V_{IL}	of IL	
V_{U0}	Initial U particle	$P_{U0}\upsilon_U$
V	total	$V_{FP} + V_{IL}$
Concentrations mol/cm^3		
j	Al extracted from the matrix by one U atom in the IL	
m	Al atoms from the IL to extract one atom of U from the FP	2
n_{Al}	Al in the IL	xn'_U
n_{Al0}	pure Al	
n_{U0}	pure U	$P_{U0}/V_{U0} = (v_U)^{-1}$
n_{fpp}	fpp in FP	N_{fpp}/V_{FP}
n_U	U in FP	N_U/V_{FP}
n'_{fpp}	fpp in IL	N'_{fpp}/V_{IL}
n'_U	U in IL	N'_U/V_{IL}
x	Al/U ratio	
x_A	Al/U ratio in the IL at interface A	~ 3
x_B	Al/U ratio in the IL at interface B	4
x_{Aeq}	equilibrium Al/U ratio of phase in contact with pure U	4
x_{Beq}	equilibrium Al/U ratio of phase in contact with pure Al	2
Lengths		
R_A	radius of FP	
R_{A0}	initial radius of FP	25 µm
R_B	radius of FP + IL	
X	dimensionless radius of FP	R_A/R_{A0}
Y	dimensionless radius of FP + IL	R_B/R_{A0}
Physical properties		
D	diffusivity of Al in the IL	see Section 12
G	integration constant	see Eq. (9)
j_U	flux of U from FP to IL	see Eq. (14)
j_{fpp}	flux of fpp from FP to IL	
K	dimensionless constant	K/R_{A0}
K'	integration constant	see Eq. (9)
k_A	rate constant at interface A	Eq. (10a)
k_B	rate constant at interface B	Eq. (10b)
Q_A	ratio of characteristic times	t_A/t_D
Q_B	ratio of characteristic times	t_B/t_D
s	fiss. prod. swelling coefficient in FP	
s'	fiss. prod. swelling coefficient in IL	
S	fractional swelling	Section 5
t	time	s
t_A	characteristic time of rxn at A	s
t_B	characteristic time of rxn at B	s
t_D	characteristic diffusion time	s
t_{235}	e-folding time of U-235	s
T	temperature	400 K
Ω	ratio of characteristic times	t_{235}/t_D
Z	dimensionless ratio	Eq. (23)

Because of the greater enrichment of dispersion fuel (20%) than oxide fuel of LWRs (<5%), generation of Pu-239 from U-238 need not be considered. In this analysis, the neutrons are of no interest and so are omitted from the above reactions.

2. Effect of burnup

At any time during irradiation, the total quantity of uranium (in IL + FP) exists in the three isotopic forms U-235, U-236 and U-238. This total is expressed as follows:

$$\begin{aligned} P_U &= P_{235} + P_{236} + P_{238} \\ &= e \times P_{U0}(1 - bu) + e \times bu \times P_{U0} \times \gamma + (1 - e)P_{U0}, \end{aligned} \tag{1}$$

where e is the initial U-235 enrichment of the fuel particle, γ is the ratio of the absorption and total cross sections of U-235 and bu is the fraction of U-235 consumed. Eq. (1) can be written in compact form as

$$P_U/P_{U0} = 1 - E, \tag{1a}$$

where

$$E = e \times bu \times (1 - \gamma), \tag{2}$$

E is an alternate burnup measure termed FIMA (fissions per initial metal atom).

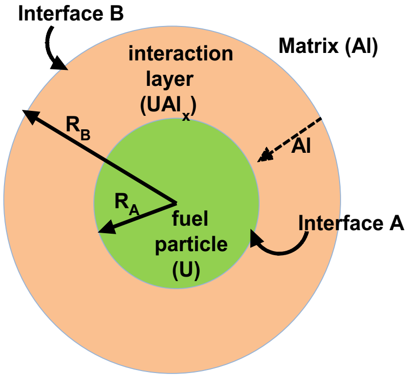

Fig. 1. Reaction of a spherical uranium fuel particle in an aluminum matrix.

The total moles of fission-product pairs (fpp) is given by

$$P_{fpp} = e \times P_{U0}(1-\gamma) \times bu \text{ or } P_{fpp}/P_{U0} = E. \tag{3}$$

3. Volumes of the FP and the IL

Since the growth of the IL thickness with burnup is related to its volume, it is necessary to express the volumes of the two phases in terms of the previously-defined quantities. Thus, the volume of the FP is given by

$$V_{FP} = N_U \times v_U + N_{fpp} \times \beta \times v_U = v_U \times f \times (P_U + \beta P_{fpp}).$$

Here N_U and N_{fpp} are the moles of U and fission-product pairs in the FP, respectively and v_U is the molar volume of U in the FP (assumed to be independent of burnup). β is the ratio of the molar volumes of the fpps and U in the FP and f is the fraction of the total uranium (or the total fpp) in the FP.

Using Eqs. (1a) and (3) and the identity $V_{U0} = P_{U0}v_U$, the above equation becomes:

$$V_{FP}/V_{U0} = [1 + (\beta - 1) \times E] \times f. \tag{4a}$$

Similarly, for the IL

$$V_{IL}/V_{U0} = H \times [1 + (\beta' - 1) \times E] \times (1 - f). \tag{4b}$$

Here H is the Pilling–Bedworth ratio of uranium in the IL and FP and β' is the ratio of the molar volumes of the fpps and U in the IL.

4. Concentrations of U

In the FP, the U concentration is

$$n_U = \frac{N_U}{V_{FP}} = \frac{f \times P_{U0}(1-E)}{V_0[1 + (\beta - 1)E] \times f}$$

or

$$\frac{n_U}{n_{U0}} = \frac{1-E}{1 + (\beta - 1)E}, \tag{5a}$$

where N_U has been expressed as $f \times P_U$, P_U in terms of Eq. (1a) and n_U by Eq. (5a). V_{FP} was replaced by Eq. (4a) and $P_{U0} = n_{U0} \times V_{U0}$. The corresponding ratio in the IL is

$$\frac{n'_U}{n_{U0}} = \frac{1-E}{H \times [1 + (\beta' - 1)E]}. \tag{5b}$$

5. Fission-product swelling

As shown below, the coefficients β and β' are directly related to the fission-product swelling coefficients in the FP and the IL, respectively.

Consider 1 mol of U metal isolated from its environment. The initial volume of the 1 mol of U is v_U. With burnup, the 1 mol is divided into $(1 - E)$ moles of U and E moles of fission product pairs. The volume after U burnup E is

$$V = (1-E) \times v_U + E \times \beta \times v_U = [1 + (\beta - 1) \times E] \times v_U$$

The fractional swelling, denoted by S, is defined by

$$S = V/v_U - 1$$

Replacing the right-hand side of this equation by the previous equation yields:

$$S = (\beta - 1) \times E$$

For swelling that increases linearly with burnup, $S = s \times bu$, where s is the swelling coefficient. Eliminating S and substituting E from Eq. (2) in the above equation yields:

$$\beta = 1 + \frac{s}{e \times (1-\gamma)}. \tag{6a}$$

The analogous result for the IL is

$$\beta' = 1 + \frac{s'}{e \times (1-\gamma)}. \tag{6b}$$

Thus, knowledge of s and s' fixes the molar-volume ratios β and β'. If s or s' changes at a particular burnup, it is because the molar volume of the fpps has changed.[1]

6. Interface processes

At interface A in Fig. 1, Al in the IL reacts with U in the FP to form the intermetallic compound:

$$U(FP) + mAl(IL) \rightarrow UAl_{x_A}(IL), \tag{7a}$$

m is the number of Al atoms in the IL at interface A that are required to extract one U atom from the FP. The rate at which Al is supplied to the IL side of interface A by diffusion equals m times the rate at which uranium is extracted from the FP by reaction (7a).

At interface B, Al from the matrix enters the IL at a rate equal to the diffusion flux towards interface A. This can be represented as the reaction:

$$U(IL) + jAl(matrix) \rightarrow UAl_{x_B}(IL), \tag{7b}$$

where x_B is the Al/U ratio in the IL at interface B. j is the number of Al atoms extracted from the matrix by a U atom in the IL.

As a result of the kinetic limitations, the Al/U ratios in the IL at interfaces A and B (x_A and x_B) differ from the equilibrium values x_{Aeq} and x_{Beq} obtained from the Al–U phase diagram (Fig. 2). The species on either side of interface A represent the two-phase $\alpha(U) + UAl_2$ region of the phase diagram. At interface B, the two-phase region is $Al + UAl_{4+x}$.

The Al/U profile in the IL is shown in Fig. 3. The difference $x_A - x_{Aeq}$ drives reaction (7a) and $x_{Beq} - x_B$ provides the driving force for process (7b). Diffusive transport of Al between the two interfaces is a result of the difference $x_B - x_A$. The process that controls the rate of IL growth can be either diffusion of Al through the IL or the rates of reactions (7a) or (7b). The analysis includes all three possibilities.

7. Aluminum diffusion in the IL

A major difference between the model used in Refs. [1] and [4] and the present model is the behavior of uranium in the IL. Rather

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[1] In U, Mo dispersion fuel, s changes at a burnup of about 55% U-235 consumed. This is believed to be due to nucleation of fission gas bubbles from dissolved atoms.

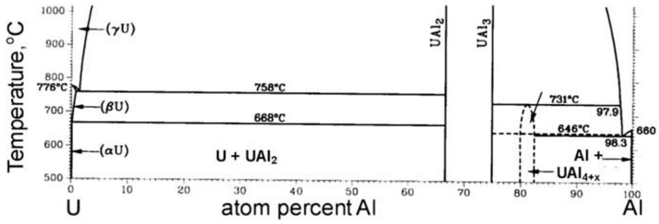

Fig. 2. Low-temperature section of the Al-U phase diagram.

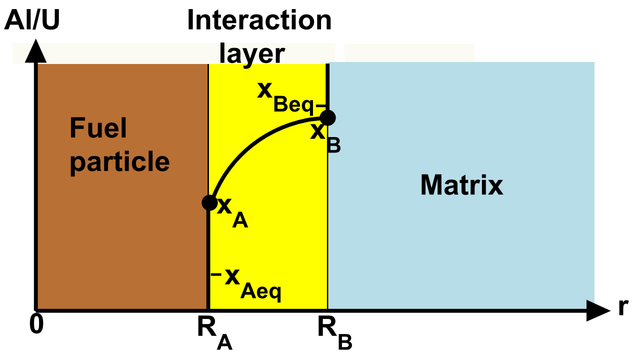

Fig. 3. Al concentration in the interaction layer.

than assuming this element to counterdiffuse with aluminum, it is considered here to be immobile. There is no diffusive flux of U relative to UAl$_x$. Outward motion of uranium is convective in nature, being generated solely by the increase in volume per U atom between the FP and the IL.[2]

In solving the diffusion equation for aluminum in the IL, the explicit time derivative is ignored. This approximation is nearly always invoked in corrosion modeling. Analysis of the Stefan problem in the Appendix shows that this approximation incurs an error of ~10%.

The diffusion equation for Al in the spherical annulus in Fig. 1 is

$$\frac{D}{r^2}\frac{d}{dr}\left(r^2\frac{dx}{dr}\right) = 0, \tag{8}$$

where D is the diffusivity of Al in UAl$_x$.[3] Integrating twice yields:

$$x = -K'/r + G, \tag{9}$$

where K' and G are integration constants.

The boundary conditions corresponding to processes (7a) and (7b), with rate constants k_A and k_B, are

$$D\left(\frac{dx}{dr}\right)_{R_A} = k_A n_U (x_A - x_{Aeq}), \tag{10a}$$

and

$$D\left(\frac{dx}{dr}\right)_{R_B} = k_B n_{Al0} (x_{Beq} - x_B), \tag{10b}$$

where n_{Al0} is the molar density of pure Al in the matrix. R_A and R_B are the radial positions of interfaces A and B, respectively.

Substituting Eq. (9) into Eqs. (10a) and (10b) yields:

$$DK'/R_A^2 = k_A n_U(-K'/R_A + G - x_{Aeq}) \text{and} DK'/R_B^2 = k_B n_{Al0}(x_{Beq} + K'/R_B - G)$$

Adding and solving for K' yields:

$$\frac{K'}{R_{A0}} = K = \frac{x_{Beq} - x_{Aeq}}{\frac{Q_A}{(n_U/n_{U0})X^2} + \frac{Q_B}{Y^2} + X^{-1} - Y^{-1}}, \tag{11}$$

where

$$Q_A = \frac{D/R_{A0}^2}{k_A n_{U0}/R_{A0}} = \frac{t_A}{t_D}, Q_B = \frac{D/R_{A0}^2}{k_B n_{Al0}/R_{A0}} = \frac{t_B}{t_D}, \tag{12a, b}$$

are the ratios of the characteristic interfacial reaction times (t_A and t_B) to the characteristic diffusion time (t_D). Also:

$$X = R_A/R_{A0} Y = R_B/R_{A0}. \tag{13}$$

The flux of Al to interface A is given by

$$D\left(\frac{dx}{dr}\right)_{R_A} n'_U = D\frac{K'}{R_A^2} n'_U$$

Since each uranium atom in the FP requires m Al atoms to be converted to UAl$_x$, the flux of uranium from the FP to the IL is

$$j_U = \frac{D}{m}\frac{K}{X^2}\frac{n'_U}{R_{A0}}. \tag{14}$$

8. Determination of *f*

The central problem is to calculate how f, the fraction of U in the FP, varies with burnup. The fundamental assumption of the analysis is that every uranium atom transferred from the FP to the IL is accompanied by two fission product atoms (i.e., a fission-product pair) in proportion to their concentrations. With Eqs. (1a) and (3), this assumption reduces to

$$\frac{j_{fpp}}{j_U} = \frac{N_{fpp}}{N_U} = \frac{E}{1-E}. \tag{15}$$

The rate of loss of total moles in the FP is

$$\frac{d(N_U + N_{fpp})}{dt} = -4\pi R_A^2 (j_U + j_{fpp}). \tag{16}$$

Using Eq. (15) and the definitions $N_U = f \times P_U$, $N_{fpp} = f \times P_{fpp}$ and $P_U + P_{fpp} = P_{U0}$, the above equation reduces to:

$$P_{U0}\frac{df}{dt} = -4\pi R_A^2 j_U (1-E)^{-1}$$

Eliminating j_U with Eq. (14):

$$P_{U0}\frac{df}{dt} = -4\pi\frac{D}{m}\frac{KR_{A0}}{1-E} n'_U$$

With n'_U given by Eq. (5b) and $V_{U0} = 4/3\pi R_{A0}^3$,

$$\frac{df}{dt} = -\frac{3}{m}\frac{(D/R_{A0}^2)K(V_0 n_{U0}/P_{U0})}{H \times [1 + (\beta' - 1)E]}$$

In the numerator, $V_{U0}n_{U0}/P_{U0} = 1$. Conversion from time to burnup in terms of the thermal neutron flux φ is accomplished by expressing the fraction of U-235 remaining as

$$\exp(-\sigma_{tot}\varphi t) = 1 - bu, \tag{17}$$

so that:

$$\frac{df}{dt} = \frac{d(bu)}{dt}\frac{df}{d(bu)} = \sigma_{tot}\varphi(1 - bu)\frac{df}{d(bu)}$$

Finally, $df/d(bu)$ is

$$\frac{df}{d(bu)} = -3\frac{\Omega}{m} \times \frac{K}{H \times [1 + (\beta' - 1)E](1 - bu)}, \tag{18}$$

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[2] This can be better seen by considering the hypothetical situation in which there is no volume change as U is converted to UAl$_x$. In this case the FP shrinks but the IL/matrix interface does not move. Hence the uranium contained in the IL is stationary.

[3] D is not a mutual diffusion coefficient, in which both members of the binary alloy are mobile. In the present situation, Al moves through stationary UAl$_x$ (see [2]).

where:

$$\Omega = \frac{D/R_{\mathrm{A0}}^2}{(\sigma_{\mathrm{tot}}\varphi)} = \frac{t_{235}}{t_D}, \tag{19}$$

is a dimensionless constant representing the ratio of the characteristic e-folding time of U-235 consumption $(1/\sigma_{\mathrm{tot}}\phi)$ to that of Al diffusion in the IL (R_{A0}^2/D).

Integration of Eq. (18) requires expression of several quantities that appear in the term K in Eq. (18). This term is defined by Eq. (11) and contains $n_{\mathrm{U}}/n_{\mathrm{U0}}$, which is defined by Eq. (5a), and the two dimensionless interface locations X and Y. These interface positions are obtained from Eqs. (4a) and (4b) by noting that $V_{\mathrm{U0}} = 4/3\pi R_{\mathrm{A0}}^3$, $V_{\mathrm{FP}} = 4/3\pi R_{\mathrm{A}}^3$ and $V_{\mathrm{IL}} = 4/3\pi(R_{\mathrm{B}}^3 - R_{\mathrm{A}}^3)$, with the results:

$$X^3 = [1 + (\beta - 1) \times E] \times f \tag{20a}$$

$$Y^3 - X^3 = H \times [1 + (\beta' - 1) \times E] \times (1 - f), \tag{20b}$$

from which X and Y are obtained as functions of f and bu.

9. Diffusion driving force

The Al/U ratios in the IL at the two interfaces ($x_{\mathrm{A}} = x(R_{\mathrm{A}})$ and $x_{\mathrm{B}} = x(R_{\mathrm{B}})$) are obtained from Eq. (9):

$$x_{\mathrm{A}} = -KX^{-1} + G \text{ and } x_{\mathrm{B}} = -KY^{-1} + G$$

subtracting gives

$$x_{\mathrm{B}} - x_{\mathrm{A}} = K(X^{-1} - Y^{-1}). \tag{21}$$

The second relation between x_{A} and x_{B} is obtained by substituting Eq. (9) into Eqs. (10a) and (10b):

$$DK'/R_{\mathrm{A}}^2 = k_{\mathrm{A}} n_{\mathrm{U}}(x_{\mathrm{A}} - x_{\mathrm{Aeq}}) \text{ and } DK'/R_{\mathrm{B}}^2 = k_{\mathrm{B}} n_{\mathrm{Al}}(x_{\mathrm{Beq}} - x_{\mathrm{B}})$$

Dividing these two equations to eliminate DK' and using Eq. (5a) yields:

$$\left(\frac{x_{\mathrm{A}} - x_{\mathrm{Aeq}}}{x_{\mathrm{Beq}} - x_{\mathrm{B}}}\right) = Z, \tag{22}$$

where

$$Z = \frac{Q_{\mathrm{A}}}{Q_{\mathrm{B}}} \frac{Y^2}{X^2} \left(\frac{1 + (\beta - 1)E}{1 - E}\right). \tag{23}$$

Solving Eqs. (21) and (22) for x_{A} gives

$$\frac{x_{\mathrm{A}} - x_{\mathrm{Aeq}}}{x_{\mathrm{Beq}} - x_{\mathrm{Aeq}}} = \frac{1 - (X^{-1} - Y^{-1})M^{-1}}{1 + Z^{-1}}, \tag{24a}$$

where M is the denominator of Eq. (11).

The analogous simultaneous solution for x_{B} gives

$$\frac{x_{\mathrm{Beq}} - x_{\mathrm{B}}}{x_{\mathrm{Beq}} - x_{\mathrm{Aeq}}} = \frac{1 - (X^{-1} - Y^{-1})M^{-1}}{1 + Z}. \tag{24b}$$

If k_{A} is very large, Eq. (12a) shows that $Q_{\mathrm{A}} \to 0$ and by Eq. (23), $Z \to 0$. The denominator of Eq. (24a) $\to\infty$ and $x_{\mathrm{A}} = x_{\mathrm{Aeq}}$. Similarly, as $k_{\mathrm{B}} \to \infty$, the kinetic resistance at interface B vanishes and $Q_{\mathrm{B}} \to 0$ and $Z \to \infty$. Hence, Eq. (24b) gives $x_{\mathrm{B}} = x_{\mathrm{Beq}}$.

10. Solution method

Eq. (18) is to be integrated with the initial condition $f = 1$ at $bu = 0$. A numerical differential-equation solver must be used.

The parameters (dimensionless) to be determined by fitting the model to IL-growth data and to the measurement of the Al/U gradient in the IL are

- Q_{A} and Q_{B} of Eqs. (12a) and (12b) and Ω of Eq. (19), or, in terms of dimensional properties, $k_{\mathrm{A}} n_{\mathrm{U0}}$, $k_{\mathrm{B}} n_{\mathrm{Al}}$ and D.

The properties employed in applying the model are

$e = 0.2$ $n_{\mathrm{U0}} = 4.8 \times 10^{22}$ U atoms/cm^3 and $R_{\mathrm{A0}} = 25$ µm; $\gamma = 0.15$
$H = 3.8$.
$s = 0.42$ for $bu < 0.55$; $s = 1.26$ for by >0.55 [5]; E from Eq. (2).
β and β' from Eqs. (6a) and (6b); $x_{\mathrm{Aeq}} = 2$; $x_{\mathrm{Beq}} = 4$ (from Fig. 2)

Assumptions include:

- $s' = s$ (i.e., equal fission-product swelling rates in the IL and the FP).
- $k_{\mathrm{B}} n_{\mathrm{Al}} = \infty$ (phase-diagram equilibrium at interface B); this gives $Q_{\mathrm{B}} = 0$ in Eq. (11).
- $m = 2$ (i.e., two Al atoms needed to extract one U atom from the FP).

The choice of m arises from the tenuous identification of this parameter with the equilibrium Al/U ratio x_{Aeq} (Fig. 2).

11. Data

11.1. In-reactor IL growth

Data for comparison of the model with experiment consist of single point from the study by Leenaers et al. [2] and a correlation of many measurements from the RERTR[4] program developed at the Argonne National Laboratory (ANL) [5]:

$$(R_{\mathrm{B}} - R_{\mathrm{A}})^2 = 5 \times 10^{-17} \dot{F} \times \exp(-3500/T)t, \tag{25}$$

R_{B} and R_{A} are in microns, T is in K and t (in seconds) is determined from the burnup using Eq. (17) and[5]

$$\dot{F} = \sigma_{\mathrm{fiss}}\varphi e n_{\mathrm{U0}} = (\sigma_{\mathrm{tot}}\varphi)(1 - \gamma)e \times n_{\mathrm{U0}} \tag{26}$$

which yields:

$$t = -(1 - \gamma)\left(\frac{e \times n_{\mathrm{U0}}}{\dot{F}}\right) \times \ln(1 - bu). \tag{27}$$

The model predictions of the IL thickness are expressed in terms of the dimensionless radii defined by Eq. (13):

$$R_{\mathrm{B}} - R_{\mathrm{A}} = R_{\mathrm{A0}}(Y - X). \tag{28}$$

The parameters in Eqs. (25) are taken to be: $\dot{F} = 8 \times 10^{14}$ cm^{-3} s^{-1} and $T = 400$ K.

11.2. Al/U ratio in the IL at interface A

For comparison of the model with measured Al/U ratios in the interaction layer (i.e., x_{A} and x_{B}), the data shown in Fig. 7(a) of Ryu et al. [1] have been used. These data suggest that at the IL/matrix interface, $x_{\mathrm{B}} \approx 4$ and consequently this parameter is fixed in the model. That $x_{\mathrm{B}} \approx x_{\mathrm{Beq}}$ indicates that the reaction at interface B is rapid, as assumed above. At the IL/FP interface, x_{A} determined by Eq. (24a) is fitted to $x_{\mathrm{A}} \approx 3$, although the Al/U gradient in the IL (Fig. 7a of Ref. [1]) suggests that x_{A} could be as large as 3.3. In either case, x_{A} is significantly larger than the phase-diagram equilibrium value, which, from Fig. 2 is $x_{\mathrm{Aeq}} = 2$.

Even though the conditions of the experiments of Ryu et al. [1] (550 °C, 5 h, unirradiated) are very different from those upon which the ANL correlation is based (<200 °C, days, irradiated), the former constitute the only datum (x_{A}) to supplement ANL's IL-thickness Eq. (25) for determining both Q_{A} and Ω.

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[4] Reduced enrichment for research and test reactors.

[5] In the ANL formula, $\dot{F}$ depends upon the power history during irradiation. For the present analysis it is taken as a constant.

11.3. Data fitting

The objective was to match data, principally the IL thickness (Eq. (25)) to the prediction (Eq. (28)), but also the Al/U ratio at interface A (x_A) to the experimental value $x_{Aexp} \approx 3$. The parameters Q_A and Ω were selected randomly and Eq. (18) integrated numerically (with $m = 2$) to give f as a function of bu. The goodness of the fit was determined by calculating the error terms:

$$\mathrm{errIL} = \frac{1}{n_{bu}} \sqrt{\sum_{n_{bu}} \left(\frac{(R_B - R_A)_{\mathrm{model}}}{(R_B - R_A)_{\mathrm{ANL}}} - 1 \right)^2}$$

$$\mathrm{errx}_A = \frac{1}{n_{bu}} \sqrt{\sum_{n_{bu}} \left(1 - \frac{(x_A)_{\mathrm{model}}}{(x_A)_{\mathrm{exp}}} \right)^2}$$

where the sums are over $n_{bu} = 8$ burnups at intervals of 0.1. The error measure minimized by the Monte Carlo search for Q_A and Ω was

$$\mathrm{err}_{\mathrm{tot}} = \sqrt{(\mathrm{errIL})^2 + (\mathrm{errx}_A)^2}. \tag{29}$$

12. Results

The minimum error was obtained with:

$$Q_A = 0.092 \pm 0.005 \text{ and } \Omega = 0.103 \pm 0.010. \tag{30}$$

With $\dot{F} = 8 \times 10^{14}$ cm^{-3} s^{-1} and the previously-defined quantities, Eq. (26) gives $\sigma_{\mathrm{tot}}\varphi = 1 \times 10^{-7}$ s^{-1}. For a $R_{A0} = 25$ µm initial FP radius, Eq. (19) results in $D = 5 \times 10^{-14}$ cm^2/s and Eq. (12a) gives $k_A n_{U0} = 2 \times 10^{-10}$ cm/s. With these values, Fig. 4 compares the model predictions with the ANL results given by Eq. (25) and Fig. 5 presents a comparison of the model predictions of the Al/U ratio at interface A with the uncertain value from Ref. [1].

13. Discussion

13.1. Rate-limiting process

$k_A n_{U0}$ is the rate constant of the reaction by which uranium is extracted from the FP to become part of the intermetallic compound in the adjacent IL. Although there is nothing with which to compare the absolute value of this quantity, the relative importance of diffusion and reaction is given by the parameter Q_A. As indicated by Eq. (12a), this quantity is the ratio of the characteristic times for reaction and diffusion. The value of Q_A determined by the fitting process indicates that $t_A \approx 10 \times t_D$, or that reaction at interface A constitutes ≈90% of the overall resistance to IL growth. This is suggested by the difference between the Al/U ratio in the IL at interface A ($x_A \approx 3$) and the equilibrium value obtained from the phase diagram ($x_{Aeq} = 2$).

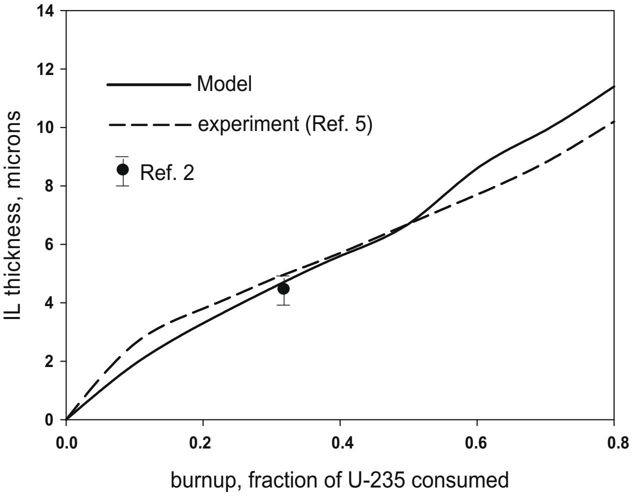

Fig. 4. Comparison of IL-growth model with experiment.

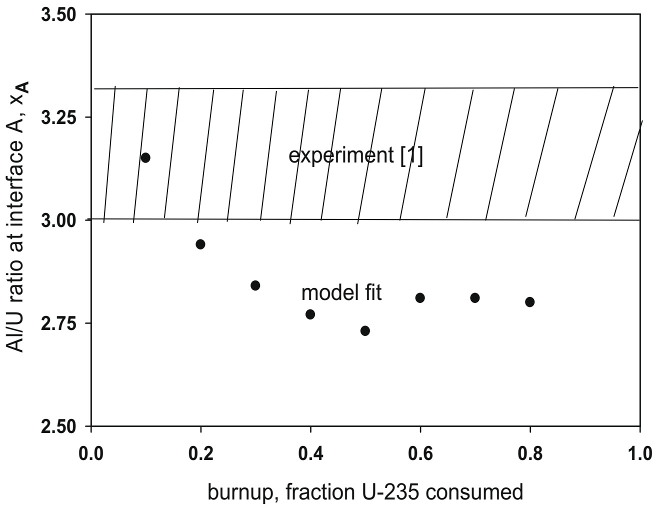

Fig. 5. Prediction of the Al/U ratio at the FP/IL interface.

The dissolution process at interface B offers no resistance to IL growth kinetics because the observed and equilibrium Al/U ratios are both ≈4.

13.2. Diffusivity of aluminum in the intermetallic compound

The diffusion coefficient obtained here by analysis of available IL-growth data ($D = 5 \times 10^{-14}$ cm^2/s) can be compared with values from the literature. From the single experiment at 550 °C, Ryu et al. [1] report 'integrated interdiffusion coefficients' for Al of 9×10^{-9} cm^2/s at 5 h and 2×10^{-8} cm^2/s at 40 h. Utilizing the same data, Soba and Denis [4] obtained 1.5×10^{-7} cm^2/s and 3×10^{-7} cm^2/s, respectively. The latter are 15 times greater than those reported in Ref. [1] and appear to be much too large; they are approaching the magnitude of diffusion coefficients in liquids.

Mehrer [6] reports the self-diffusion coefficient in pure aluminum at 550 °C as 2×10^{-9} cm^2/s, which is smaller than the integrated interdiffusion coefficients given in the preceding paragraph by factors ranging from 4 to 150. There is no known example of diffusion coefficients in an intermetallic compound greater than that of the pure metal. For example, the measured self-diffusion coefficient of Al in FeAl at 550 °C is 2×10^{-16} cm^2/s, which is 7 orders of magnitude smaller than that of the pure metal [6]. Unfortunately, the self-diffusivity of Al in UAl$_x$ with which to compare the value obtained in this work is not available in the literature. All that can be confirmed is that D determined in this study is about five orders of magnitude smaller than the self-diffusivity of Al in the pure metal. This is clearly in the right direction.

Dispersion fuels typically operate at ~400 K, so the diffusion coefficient obtained from the in-reactor data of Eq. (25) may represent a radiation-enhanced value rather than a thermal diffusivity. Matzke gives an irradiation-induced diffusivity of U in UN of 10^{-17} cm^2/s at a fission-rate density of 5×10^{12} cm^{-3}s^{-1} [7]. For $\dot{F} = 8 \times 10^{14}$, this diffusivity increases to ~2×10^{-15} cm^2/s, which is 25 times smaller than D for Al in UAl$_x$ deduced here. This discrepancy may be due to the size of the diffusing species; in UN, the diffusivity reported by Matzke is that of U, the heavier and larger of the two species. In the present case, the diffusivity is that of

Al, the lighter and smaller of the two species in the compound. If the diffusivity of U in UAl_x were known, it could very well be considerably less than that of Al in UAl_x. A better comparison would be that of *N* in UN to Al in UAl_x.

14. Pressure of released fission gas

The second objective of this work was to determine whether the pressure of fission gases released from the interaction layer (but not from the fuel) is sufficient to cause the observed plate-thickness increase (pillowing).

14.1. Fission gas in the IL

Prior to release, the total moles of fission-product pairs produced in a single fuel particle is given by Eq. (3):

$$P_{\mathrm{fpp}} == e \times P_{\mathrm{U0}}(1-\gamma) \times bu = 0.15 \times P_{\mathrm{U0}} \times bu$$

where P_{U0} is the initial quantity of uranium. According to the definition of f (Section 2), the fraction of the total fission-product pairs in the IL is $1-f$, which depends upon burnup. The fraction of the fission-product pairs attributed to fission gases (fg) is one-half of the combined yields of stable Xe and Kr, or $1/2 \times 0.26$. Therefore, the quantity of fission gas in the IL is:

$$N'_{\mathrm{fg}} = 0.02 \times P_{\mathrm{U0}} \times bu \times (1-f) \text{ moles} \qquad (31)$$

14.2. Released fission gas in the fuel plate

The plate-type fuel elements irradiated in the study of Ref. [2] consisted of a fuel-meat thickness of 0.4 mm with 0.4-mm-thick cladding on either side. After a burnup of 33% of the initial ^{235}U, 13% plate swelling (increase in plate thickness) was reported.

For the purpose of this analysis, the dimension change is approximated by the creation at the fuel element's midplane of a volume defined by two back-to-back cylinder sections with widths equal to the lateral dimension of the fuel meat. Assuming the latter to be 2 cm, Fig. 6 shows the shape that yields the appropriate swelling.

The void volume in the meat corresponding to the observed 13% swelling is the segment of the circle in Fig. 6 defined by the 20 mm chord and the 0.08 mm height. With a bit of geometry, this volume is found to be 0.011 cm^3/cm plate length.

The initial quantity of uranium in a half-thickness of the meat is calculated from the 8.5 g U/cm^3 loading reported in Ref. [2]. For the dimensions given in the first paragraph of this section, this figure corresponds to $P_{\mathrm{U0}} = 1.4 \times 10^{-3}$ mol U per cm plate length. At $bu = 0.33$, the solution of Eq. (18) yields $f = 0.84$. Inserting these values in Eq. (31) yields 1.5×10^{-6} mol fission gases in the interaction layer surrounding all fuel particles per cm of plate length.

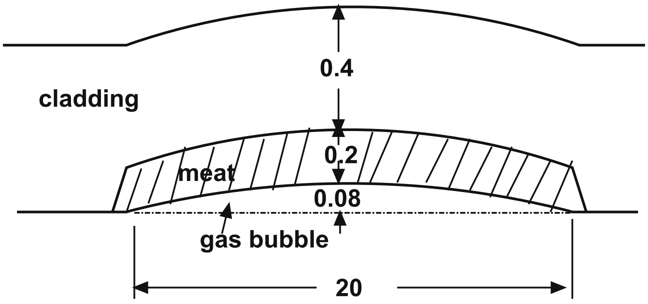

Fig. 6. Cross-section of cylindrical gas bubble representing 13% plate swelling (dimensions in millimeters).

Assuming that all of the fission gases in the IL are released to void volume of Fig. 6 and the temperature of the meat is ~200 °C, the ideal gas law yields a pressure of

$$p = \frac{(1.5 \times 10^{-6}\mathrm{mol})(82\mathrm{cm}^3 - \mathrm{atm/mol} - K) \times 473K}{0.011\mathrm{cm}^3} = 5.5\mathrm{atm}$$

It is unlikely that a pressure of this magnitude could cause yielding in the cladding.

15. Conclusions

The purpose of analyzing corrosion of the uranium particles by the aluminum matrix in dispersion fuels was twofold. The first reason was to model the growth of the interaction layer and the shrinkage of the fuel particle. The second reason, and the original motivation, was to determine whether release of all of the fission gas in the interaction layer was responsible for the often-observed swelling of dispersion-type fuel plates.

The corrosion model consisted of two series steps: diffusion of Al in the interaction layer and reaction of Al with uranium in the fuel particle. The former was viewed as migration of aluminum through stationary amorphous UAl_x. The latter considered the reaction rate at the interface to be proportional to the U concentration in the fuel particle and the Al concentration in adjacent interaction layer. Other approximations included neglect of the explicit time-dependence in the diffusion equation. Development of this model resulted in an ordinary differential equation whose solution produced the fraction of U in the FP as a function of the burnup of U-235.

The solution to the model's kinetic problem involved three dimensionless parameters: Q_A, Q_B and Ω. Q_B represents rate-limiting kinetics at the IL-matrix interface. Experimental evidence indicated this resistance to be negligible, so Q_B was set equal to zero at the outset. The other two parameters were determined by comparing the model to: (i) the empirical correlation developed at ANL for the thickness of the interaction layer as a function of time and fission-rate density; (ii) the Al concentration gradient observed in out-of-reactor experiments.

Q_A is a measure of the relative importance of reaction kinetics at interface A and Al diffusion in the IL. This parameter was found to be ~0.1, indicating that interface reaction-rate is the principal limitation of the rate of corrosion of the uranium fuel particle by the aluminum matrix in which it is embedded. The second parameter, Ω, permitted determination of the diffusion coefficient of Al through the intermetallic compound in the interaction layer. The value so determined, $D = 5 \times 10^{-14}$ cm^2/s is many orders of magnitude smaller than the values determined by two previous analyses in the literature. It is, however, consistent with self-diffusion measurements in UN, a compound with thermal and electrical conductivities similar to those of UAl_3.

The final aspect of the analysis consisted of applying the model to calculate the quantity of fission gas contained in the interaction layer and assuming that all of it was release to form a bubble. Based on observed swelling of fuel plates, the volume of the void space into which the fission gas collected could be estimated. From the number of moles of gas, the volume of the space it occupied and a typical temperature, the pressure of fission gas was calculated. This pressure was found to be much too low to deform the aluminum cladding to the extent needed to account for the observed swelling. From these results, it can be concluded that the swelling of dispersion fuel plates at high burnup is not due to collection of fission gas released to bubbles in the fuel meat.

A possible cause of blistering (pillowing) is mechanical failure at the midplane of the fuel meat due to tensile stress normal to the plate. The origin of this stress may be the difference in the expansion coefficients (both thermal and fission-product) between fuel meat and the cladding. The neutron flux gradient in the plate and the restraints from the plate holders may also contribute to the stress responsible for separation of the fuel meat.

Appendix
The moving-boundary effect

The analysis in the text ignored the explicit time derivative in the diffusion equation and the effect of the movement of interface A. Incorporation of these effects was first analyzed by Stefan in 1891 to describe the growth of an ice layer on freezing water [8]. In order to assess the effect of this simplification of the problem, Cartesian rather than spherical geometry is analyzed.

The unsteady-state diffusion equation for transport of Al through the U matrix is

$$\frac{\partial x}{\partial t} = D\frac{\partial^2 x}{\partial z^2} \tag{A.1}$$

where x is the Al/U mol ratio and z is the distance into the IL measured from the IL/matrix interface (B). With $\delta(t)$ the thickness of the IL, the initial and boundary conditions are

$$\delta(0) = 0; \quad x(0,t) = x_B = 4; \quad x(\delta,t) = x_A = 3 \tag{A.2}$$

The IL growth rate is related to the flux of Al at the FP/IL interface (A)[6]

$$-D\left(\frac{\partial x}{\partial z}\right)_{z=\delta} = x_A\frac{d\delta}{dt} \tag{A.3}$$

The solution to Eq. (A.1) taking Eqs. (A.2) and (A.3) into account is [8]:

$$\delta^2 = 4\mu^2 Dt \tag{A.4}$$

μ is a dimensionless quantity given by

$$\mu e^{\mu^2} erf(\mu) = 1/2\frac{x_B - x_A}{x_A} = 0.167 \tag{A.5}$$

Solving Eq. (A.5) yields $\mu = 0.365$ and Eq. (A.4) reduces to

$$\delta = 0.74\sqrt{Dt} \tag{A.6}$$

If the concentration gradient is assumed to be constant at the outset (i.e., the time derivative in Eq. (A.1) is ignored), the solution is

$$\delta = \sqrt{2}\left(\frac{x_B - x_A}{x_A}\right)^{1/2}\sqrt{Dt} = 0.82\sqrt{Dt} \tag{A.7}$$

Comparison of Eqs. (A.6) and (A.7) shows that the error incurred by neglecting the moving-boundary aspect of the problem is ~10%.

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[6] Eq. (A.3) is the analog of Eq. (16) in the text.