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An investigation of the Pu migration phenomena during irradiation in fast reactor

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Abstract

The phenomenon of radial plutonium migration in fast reactor MOX fuel is one of the important performance issues. In this study, mechanisms of this phenomenon were modeled for vapor transport concurrently occurring with thermal diffusion. Further improvement was modeled by accounting for the effects of the oxygen to metal ratio. Additionally, to evaluate more precisely the fuel temperature history during irradiation, the thermal conductivity in the fuel-cladding gap was evaluated by including the thermal effects of fission-product (FP) compounds. The calculated plutonium distribution in MOX fuel irradiation tests, with the linear heat rate (LHR) gradually decreasing with irradiation, agreed well with the measured data. Improvement by considering the effect of the oxygen to metal ratio was considered to be effective and indispensable for the evaluation of plutonium migration in the MOX fuel. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is well known that in hypostoichiometric uranium–plutonium mixed oxide (MOX) fuel the Pu migrates against the temperature gradient during irradiation, particularly in the radial direction under high-temperature gradients. This migration leads to local Pu concentration variations that affect the fuel thermal properties. For commercial FBR MOX fuel, the impact on the fuel thermal performance may be considerable.

Many investigations have been conducted on this phenomenon and significant fundamental information on Pu migration mechanisms have been obtained. Bober and Schumacher [1] and Matzke [2,3] (representative examples) found that vapor transport and thermal diffusion are the dominant mechanisms and that the temperature, oxygen to metal (O/M) ratio, and Pu content would markedly affect these transport mechanisms. However, based on the results of Pu migration evaluations, the difference between the evaluated distributions and the measured data, obtained by post-irradiation examinations, is significant. The main discrepancy appears to be caused by an uncertainty in the evaluation of fuel temperature history, but also partly by limitations in the modeling of Pu migration.

In this study, the effect of the O/M ratio on Pu migration was taken into account, as well as improvements in the evaluation model for the fuel temperature history by considering the effect of fission-product (FP) compounds in the fuel-cladding gap. These improvements were applied to the fuel performance analysis code 'CEDAR' [4], which was developed by JNC, to evaluate Pu migration in a fuel pin system.

2. Models

2.1. Model of Pu migration

In this study, the Pu migration was modeled with thermal diffusion concurrently occurring with vapor

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transport via pores in the fuel. The paths for vapor transport in fuel are pores and cracks that transverse the fuel from the central void to the periphery [1–3,5] (representative examples). However, these cracks heal relatively fast during irradiation, and thus their contribution to the vapor transport should thus be negligible. Therefore, only pores were considered as paths for the vapor transport.

The Pu migration equation is expressed according to Fick's second law:

$$\frac{\partial C}{\partial t} = -\nabla J, \tag{2.1}$$

where C and J are the fractional concentration and transport flux of Pu, respectively, and t is time. The equation used for J is as follows:

$$J = J_{\mathrm{sol}} + J_{\mathrm{pore}}, \tag{2.2}$$

where J_{sol} is the Pu flux by thermal diffusion and J_{pore} by vapor transport via pores. The equation used for the flux J_{sol} is as follows [1]:

$$J_{\mathrm{sol}} = -\tilde{D}\left\{\frac{\partial C}{\partial r} + C(1-C)\frac{Q^*}{RT^2}\frac{\mathrm{d}T}{\mathrm{d}r}\right\}, \tag{2.3}$$

where $\tilde{D}$, Q^*, T, R, and r are the U–Pu interdiffusion coefficients, heat of transport, temperature, gas constant, and radial position, respectively. In this study, Q^* is taken to be $-35\,000$ cal/mol [1].

The equation used for the flux J_{pore} was adopted from Clement and Finnis [5]:

$$J_{\mathrm{pore}} = -P\frac{\tilde{D}}{d}\frac{\vec{v}}{v}\,\delta C\exp\left(-\frac{\tilde{D}}{l\,v}\right), \tag{2.4.1}$$

where P, v, d, and l are the porosity, pore velocity, pore thickness, and pore diameter, respectively. For d and l the dimensions 0.008 and 80 mm [5] were applied. δC is the change in the Pu content by vapor transport via pores and is expressed as follows [5]:

$$\delta C = A_1\, l\, C\left|\frac{\mathrm{d}T}{\mathrm{d}r}\right|, \tag{2.4.2}$$

where A_1 is a constant. In the above expression, the pores are assumed to be circular cylinders of thickness d and diameter l [5].

2.2. U–Pu interdiffusion coefficient

The U–Pu interdiffusion coefficient was assumed to primarily depend on the temperature and chemical conditions in the fuel, such as Pu content and O/M ratio.

However, the applicable data for determining in detail the dependence of the U–Pu interdiffusion coefficient on chemical conditions are very limited and the evaluation models for such dependences have not been established.

Therefore, in this study, we planned to model the O/M ratio dependence of the U–Pu interdiffusion coefficient and the following equation is used:

$$\tilde{D} = F(\mathrm{OM})\tilde{D}_{\mathrm{sto}}, \tag{2.5.1}$$

$$\tilde{D}_{\mathrm{sto}} = A_2\exp\left(\frac{-Q^*}{RT}\right), \tag{2.5.2}$$

where A_2 is a constant and the function $F(\mathrm{OM})$ is the dependence of the interdiffusion coefficient on the O/M ratio. $\tilde{D}_{\mathrm{sto}}$ means the U–Pu interdiffusion coefficient in stoichiometric MOX and Q^* is the activation energy. In this study, Q^* is taken to be $-130\,000$ cal/mol [6].

With respect to the Pu content dependence of the interdiffusion coefficient, $\tilde{D}_{\mathrm{sto}}$ is considered to be expressed as follows:

$$\tilde{D}_{\mathrm{sto}} = CD_{\mathrm{U}} + (1-C)D_{\mathrm{Pu}}, \tag{2.6}$$

where D_{U} and D_{Pu} are the intrinsic diffusion coefficients in MOX with a Pu content of C. However, there are a few data for the U and Pu intrinsic diffusion coefficients in MOX. Therefore, in this study, it was assumed that D_{Pu} would be equal to D_{U}, and the Pu content dependence of the interdiffusion coefficient was not taken into account.

The functional dependence $F(\mathrm{OM})$ of the O/M ratio considers the relationship between the dependence of the interdiffusion coefficient and the concentration of the lattice defects, viz., vacancies located at the metal atoms sites or interstitial metal atoms [2,3] (representative examples). In the lower hypostoichiometric region the dominant defects should be the interstitials. At higher O/M ratios, the concentration of interstitials is lower, implying that the dominant defects can change from interstitial atoms to vacancies. Thus, the functional dependence $F(\mathrm{OM})$ is proportional to the concentration of interstitials in the lower hypostoichiometric region and vacancies in the higher hypostoichiometric region.

Based on this consideration and data from Matzke [2,3] (representative examples), change in the coefficient with O/M in the hypostoichiometric region was modeled as follows:

$$\begin{aligned} F(\mathrm{OM}) &= N_{\mathrm{LD}}(\mathrm{OM}=1.94)/N_{\mathrm{LD}}(\mathrm{OM}=2.00), \\ &\qquad \mathrm{OM} \leqq 1.94 \\ &= (a), \quad 1.94 < \mathrm{OM} < \mathrm{OM_{TH}} \\ &= N_{\mathrm{LD}}(\mathrm{OM}=\mathrm{OM_{TH}})/N_{\mathrm{LD}}(\mathrm{OM}=2.00), \\ &\qquad \mathrm{OM} = \mathrm{OM_{TH}} \\ &= (a), \quad \mathrm{OM_{TH}} < \mathrm{OM} < 2.00 \\ &= 1.00, \quad \mathrm{OM} = 2.00. \end{aligned} \tag{2.7.1}$$

The linear interpolation of (a) in common logarithm form is due to the fitting of the Matzke data [2,3] (rep-

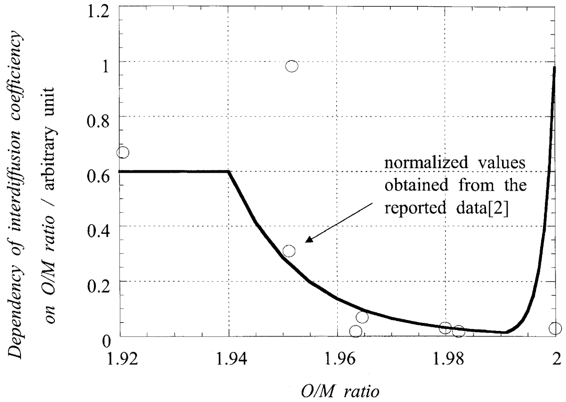

Fig. 1. Calculated O/M ratio dependence of the U–Pu interdiffusion coefficient at 1773 K.

resentative examples). The $N_{\mathrm{LD}}(\mathrm{OM})$ was expressed as follows [2,3] (representative examples):

$$N_{\mathrm{LD}}(\mathrm{OM} = 1.94) = 0.0009\exp(-3.1[\mathrm{eV}]/k_{\mathrm{B}}T), \quad (2.7.2)$$

$$N_{\mathrm{LD}}(\mathrm{OM} = \mathrm{OM}_{\mathrm{TH}}) = \{4/(2.00 - \mathrm{OM}_{\mathrm{TH}})^2\}\exp(-6.4[\mathrm{eV}]/k_{\mathrm{B}}T), \quad (2.7.3)$$

$$N_{\mathrm{LD}}(\mathrm{OM} = 2.00) = 2\exp(A_3/k_{\mathrm{B}}T), \quad (2.7.4)$$

$$\mathrm{OM}_{\mathrm{TH}} = 2.00 - \{16\exp(-3.3[\mathrm{eV}]/k_{\mathrm{B}}T)\}^{1/4}, \quad (2.7.5)$$

where the constant A_3 is from the calculations of Pu migration data in irradiated fuels by the CEDAR code and K_{B} is the Boltzmann constant. Fig. 1 shows the calculated O/M ratio dependence of the U–Pu interdiffusion coefficient at 1773 K with the normalized reported data [2,3] (representative examples).

2.3. Model of the thermal conductivity in the fuel-cladding gap

In irradiation tests of high burnup fuel, there is a considerable amount of various compounds in the fuel-cladding gap. Since these compounds can significantly affect the thermal conductivity in the gap, it was necessary to consider this fact to evaluate more precisely the fuel temperature. Also, in the same fuel-cladding gap, there are gases such as He, Xe, and Kr. The gap thermal conductivity is influenced by both the heat transfer through solids and through gases. The following expressions for the thermal conductivity of the mixtures of solid and gaseous materials [7] are used:

$$K = \left\{\frac{C}{k_{\mathrm{A}}} + \frac{(1-C)}{K_{\mathrm{B}}}\right\}^{-1}, \quad (2.8.1)$$

$$k_{\mathrm{A}} = (1-\varepsilon)K_{\mathrm{s}} + \varepsilon K_{\mathrm{g}}, \quad (2.8.2)$$

and

$$K_{\mathrm{B}} = \left\{\frac{(1-\varepsilon)}{K_{\mathrm{s}}} + \frac{\varepsilon}{K_{\mathrm{g}}}\right\}^{-1}, \quad (2.8.3)$$

where C is constant and ε is the fractional volume of the gaseous material, i.e., porosity. K_{s} and K_{g} are the thermal conductivities of solid and gaseous materials, respectively.

It was assumed that cesium molybdate Cs_2MoO_4 would be representative of gap compounds, particularly from the viewpoint of thermal conductivity. Therefore, the fuel-cladding gap was assumed to consist of Cs_2MoO_4, He, and the FP gases Kr and Xe.

Thus, the following equations are used:

$$K = \left\{\frac{0.8}{K_{\mathrm{A}}} + \frac{0.2}{K_{\mathrm{B}}}\right\}^{-1}, \quad (2.9.1)$$

where the constant C in Eq. (2.8.1) is taken to be 0.8, which is applied to a packed bed by fine fragments like sand [7]. k_{A} and k_{B} are expressed as follows:

$$K_A = (1-\varepsilon)K_{\mathrm{FP}} + \varepsilon K_{\mathrm{Gas}} \quad (2.9.2)$$

and

$$K_B = \left\{\frac{(1-\varepsilon)}{K_{\mathrm{FP}}} + \frac{\varepsilon}{K_{\mathrm{Gas}}}\right\}^{-1}. \quad (2.9.3)$$

The following expression is used for ε:

$$\varepsilon = \frac{V_{\mathrm{FP}}}{V_{\mathrm{gap}}}, \quad (2.9.4)$$

where the volume of FP compounds V_{FP} is expressed as follows:

$$V_{\mathrm{FP}} = \frac{(0.5Y_{\mathrm{Cs}}BU)}{\rho_{\mathrm{FP}}}, \quad (2.9.5)$$

where V_{gap}, Y_{Cs}, ρ_{FP}, BU are the volume of gap, yield of Cs, mol volume of FP compound (104 cc/mol of Cs_2MoO_4 with 94%TD [8]), and burnup, respectively. K_{Gas} is the thermal conductivity of a mixture of gases (He, Kr, and Xe) in the gap. The expression for K_{FP} of FP compounds is assumed to be as follows [8]:

$$K_{\mathrm{FP}} = 0.01\left(\frac{78.24}{T} + 0.15 + 1.7\times10^{-10}T\right) \quad \text{for } T < 845[\mathrm{K}],$$
$$= 0.01\left(\frac{132.56}{T} + 0.03 + 3.2\times10^{-10}T\right). \quad (2.10)$$

Fig. 2 shows the calculated temperatures in the radial direction at end of life (EOL) of the $(U_{0.7}Pu_{0.3})O_{1.96}$ fuel irradiated to a burnup of about 130 GWd/t, at a linear

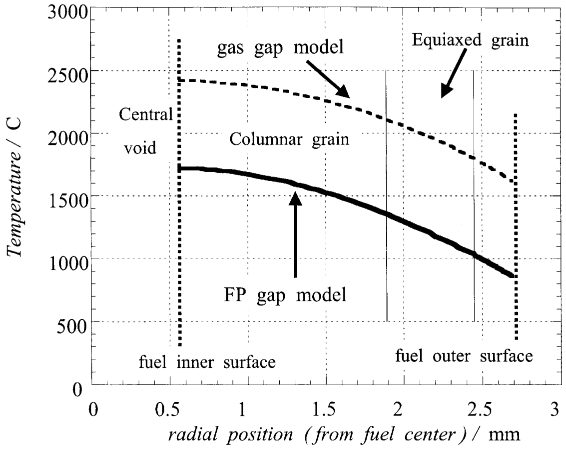

Fig. 2. Radial temperature distributions at EOL calculated by the gas gap model and by the FP gap model (BU = 13 at.%, LHR at EOL = 300 W/cm).

heat rating of 260 W/cm at EOL, and a residual gap width (radius) of 110 μm. The solid line ('FP gap model') shows the result by the above model, and the dashed line ('gas gap model') shows the result by the model which assumes that only gases exist in the gap. In this figure, the restructuring areas obtained by ceramography tests at PIE are also shown. It is considered from Fig. 2 that the 'gas gap model' overestimates the temperature; also the effect of FP compounds seems to be indispensable for temperature evaluation.

2.4. Synthesis of Pu migration analysis

The fuel performance analysis code CEDAR [4] is an R–Z system code for evaluating the fuel thermal conditions during irradiation, such as central void formation caused by pore migration, and oxygen migration.

New models for Pu migration and thermal conductivity of the gap were added to this code. The unknown constants A_1, A_2, and A_3 could be determined based on the calculations by this modified CEDAR code.

3. Results and discussion

3.1. Pu distribution data

The constants A_1, A_2, and A_3 could be fixed by comparing the calculated Pu distributions by the CEDAR code with the measured data from various irradiated MOX solid pellets, which had been fabricated by JNC and had an O/M ratio of 1.95–1.99 and a Pu content of 27–30 wt%. The fuel burnup ranged from near 0 to 110 GWd/t with the linear heat rate (LHR) gradually decreasing with irradiation. The data of Pu distributions were obtained by EPMA.

In this paper, the calculation results of the specimens XD0992 and XD1071 are described. XD0992 and XD1071 were obtained from 560 effective full power days (EFPD) irradiation test, with its initial O/M ratio of 1.99 and 1.955 and initial Pu content of 27 and 30 wt%, which had achieved an estimated burnup of 106 and 110 GWd/t, respectively. Although these specimens were obtained from different pins, the irradiation conditions were almost the same; their LHR at beginning of life (BOL) corresponds to about 440 W/cm. However, the amounts of Pu enrichment due to Pu migration in the vicinity of the central void in these specimens are apparently different.

3.2. Results and discussion

The value of the constants A_2 in Eq. (2.5.1) and A_3 in Eq. (2.7.4) is found to be 2.0×10^3 and −4.2 eV. For A_1 in Eq. (2.4.2) the value is 5.00 with the condition of $(b) < 99.7\%$TD and 0.65 with $(b) \geqq 99.7\%$TD, where (b) is the average fuel density in the vicinity of the central void. The basis for the above values of A_1 is described next.

It is considered from the calculation results by the CEDAR code that the density in the vicinity of the central void, the columnar grain region, tends to increase rapidly up to about 99.7%TD; thereafter the increase occurs very slowly. Based on qualitative investigations of pore migration, the density increases by the movement of lenticular pores with the formation of the highly dense region; i.e., columnar grain region. On the other hand, in this highly dense region, the shape of residual pores appears to be non-lenticular. Therefore, the rapid increment of densification appears to be

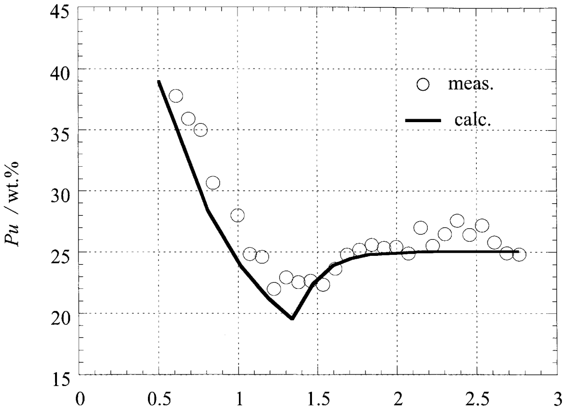

Fig. 3. Radial Pu distribution of XD0992 obtained from PIE (initial O/M = 1.99, initial Pu = 27 wt%).

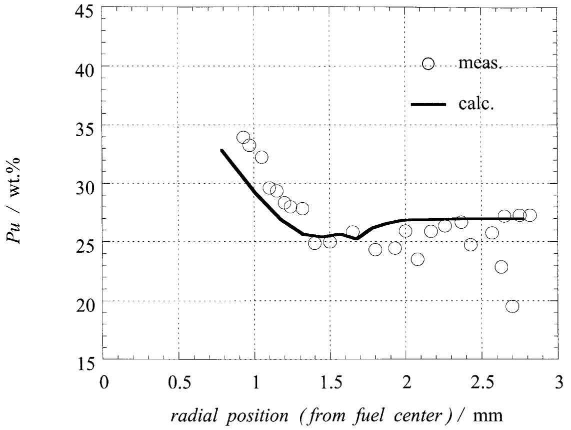

Fig. 4. Radial Pu distribution of XD1071 obtained from PIE (initial O/M = 1.955, initial Pu = 30 wt%).

caused by porosity moving via lenticular pores and the slow increments by fine spherical pores. Since it is easily obtained from Eq. (2.4.2) that the shape of the moving porosity can affect the amount of U and Pu transport, the value of A_1 was assumed to change with the average density in the vicinity of the central void, and its threshold density was set at 99.7%TD.

The results of the radial Pu migration calculations are shown in Fig. 3 (XD0992) and Fig. 4 (XD1071).

It is apparent in Figs. 3 and 4 that the calculated radial Pu distribution shows good agreement with the measured data. Since the initial O/M ratio was different in these specimens, it can be concluded that the dependence of Pu migration on the O/M ratio was modeled well.

4. Conclusions

This conclusion is based on calculations and qualitative considerations in the fuel with the condition that LHR decreases with irradiation and breeding has not occurred.

The Pu migration in MOX fuel pellets was investigated by including the effects of the O/M ratio.

These variables were modeled and added to the FBR MOX fuel performance code CEDAR and the calculated plutonium distributions by CEDAR code agreed well with the measured data.

The improvement of this study by considering the effect of the O/M ratio was considered to be effective and indispensable for the evaluation of plutonium migration in MOX fuel.

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