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# The stoichiometry and the oxygen potential change of urania fuels during irradiation

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**Abstract**

A defect model for irradiated $UO_2$ fuel solid–solution was devised based on the defect structure of pure urania. Using the equilibrium between fuel solid–solution and fission-products and the material balance within the fuel, the stoichiometry change of urania fuel was traced with burn-up. This tracing method was applied to high burn-up fuels. The oxygen potential of urania fuel turned out to increase slightly with burn-up. The stoichiometric change was calculated to be negligible due to the buffering role of Mo. © 1997 Elsevier Science B.V.

## 1. Introduction

Nuclear fuel performance strongly depends on the stoichiometry of the fuel. The diffusion coefficient of fission gases and the thermal conductivity of the fuel matrix are affected by the fuel stoichiometry change [1,2]. Fuel stoichiometry may change during irradiation due to the appearance of fission products (fp's). While the oxygen potential of the fuel determines the chemical states of fp's, the oxygen potential of the fuel is also influenced by soluble fp's in the fuel matrix.

Economical use of nuclear fuels makes a trend for the extended burn-up, nowadays. High burn-up fuel contains lots of fp's affecting the stoichiometry of the fuel and also the performance. For that reason, the stoichiometric change of high burn-up fuels becomes of important concern. In this paper, a defect model for the oxygen potential of urania fuel containing fp's is devised, and is applied to the estimation of the oxygen potential change of urania fuel at high burn-up.

## 2. Oxygen potential of irradiated fuel

### 2.1. Chemical state of fission products

Table 1 illustrates the chemical states of fp's in groups. Xe and Kr are inert gases, and Br and I have high vapor pressures with the possible formation of CsI. Cs is very reactive, and forms somewhat complicated compounds with U, Mo and O. Mo, Tc, Ru, Rh and Pd are the main metallic elements. Ag, Cd, In, Sn, Sb and Te also exist as metals, but their low vapor pressures make them observed in the vicinity of pores and gaps between pellets and cladding. Nd, La, Y, Nd, Sm, Eu, Gd, Pm, Zr, Ce and Pr form solid solutions with the $UO_2$ fuel. The fission yield of each elemental group is obtained from the calculation of ORIGEN-2 [12].

### 2.2. The oxygen potential of urania fuel containing soluble fission products

The oxygen potential of the urania fuel with soluble fp's is modeled based on the defect structure of pure urania [3]. Since fp's are composed by many elements, grouping of fp's is necessary. We divide the soluble fp's into three groups. Pu, Ln and Zr groups, depending on their valences in the fuel, as shown in Table 2. Pu, Ce are

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Table 1
Elements and chemical state of each group of fission products

| Elements | Chemical states | Notation |
|---|---|---|
| Xe, Kr | noble gas | Xe |
| Br, I | volatiles | Br |
| Rb, Cs | reactive, CS–U–O, Cs–Mo–O | Cs |
| Mo, Te, Ru, Rh, Tc | metal, Mo can be oxide | M |
| Ag, Cd, In, Sn, Sb | metal (low melting temp.) | Cd |
| Ba | oxide precipitates | Ba |
| Nd, La, Y, Nd, Sm, Eu, Gd, Pm, Zr, Ce, Pr | soluble to fuel matrix | Ln |

very soluble to urania. In the hypostoichiometric region, most Pu ions are known to be reduced to meet the charge neutrality. The solubility of Zr in urania is not high, but when mixed with rare earth elements, the solubility increases. The oxygen potential of urania is measured to be slightly lower than that of pure urania with Zr in it [4]. However, the Zr concentration may exceed the solubility limit and the values measured by Aronson may not be reliable [5]. Hence, we assume that Zr does not give any effect on the oxygen potential except staying on the metal site with the valence of +4. Rare earth elements, Nd, La, Sm and Y exist in urania with the valence of +3. They generally increase the oxygen potential of the fuel solid solution.

A defect model for the oxygen potential of the urania fuel containing fp's is made based on the defect structures of doped urania [6,7]. The assumed modeling is as follows:

(i) The basic defect structure of pure urania is applicable [6].

(ii) The factor for the anion site reduction due to the addition of dopants is the same as that of Nd-doped urania [7].

(iii) Pu group elements make an equilibrium with uranium ions

$$\mathrm{Pu}_{\mathrm{U}}^{x} + \mathrm{U}_{\mathrm{U}}^{x} = \mathrm{Pu}'_{\mathrm{U}} + \mathrm{U}_{\mathrm{U}}^{\cdot}: \quad K_{\mathrm{P}}. \tag{1}$$

(iv) $\mathrm{Ln}'_{\mathrm{U}}$ forms a vacancy cluster with *U* positive polarons and oxygen vacancies

$$\mathrm{V}_{\mathrm{O}}^{\cdot\cdot} + 4\mathrm{U}_{\mathrm{U}}^{x} + 2\mathrm{Ln}'_{\mathrm{U}} + \mathrm{U}_{\mathrm{U}}^{\cdot} = (5\mathrm{U{:}V{:}2Ln})^{\cdot}: \quad K_{\mathrm{I}}. \tag{2}$$

Table 2
Grouping of soluble fp's and their valence in fuel solid solution

| Element | Valence | Characteristics |
|---|---|---|
| Pu, Ce, Pr | +3, +4 | mainly +4:<br>reducing condition +3 |
| Nd, La, Y, Nb, Sm, Eu, Gd, Pm | +3 | always +3 |
| Zr, Mo | +4 | mainly +4 |

Table 3
Equilibrium constants of defect reactions

| Temperature (K) | ln $K_{\mathrm{B}}$ | ln $K_{\mathrm{P}}$ | ln $K_{\mathrm{I}}$ | ln $K_{\mathrm{N}}$ |
|---|---|---|---|---|
| 1273 | 9 | −8.4 | 15 | 13 |
| 1573 | 2 | −7.1 | 11 | 11 |

(v) $\mathrm{LN}'_{\mathrm{U}}$ makes a cluster with oxygen interstitials and U positive polarons and oxygen interstitials

$$\mathrm{O}_{\mathrm{i}}'' + 2\mathrm{U}_{\mathrm{U}}^{\cdot} + \mathrm{Ln}'_{\mathrm{U}} = (2\mathrm{U{:}O{:}Ln})': \quad K_{\mathrm{N}}. \tag{3}$$

(vi) $\mathrm{Ln}'_{\mathrm{U}}$ partially forms a pair with an U positive polaron

$$\mathrm{U}_{\mathrm{U}}^{\cdot} + \mathrm{LN}'_{\mathrm{U}} = (\mathrm{U{:}Ln}): \quad K_{\mathrm{B}}. \tag{4}$$

(vii) The numbers of sites for both cations and anions are conserved and material balance for oxygen to metal ratio (O/M) and the charge neutrality have to be met.

The oxygen potential data of irradiated nuclear fuels that are comparable to this model are rare. Une and Oguam have measured the oxygen potential of simulated urania fuel with respect to nonstoichiometry at 1273 and 1573 K [8]. We compared Une and Oguma's results with this model to find the equilibrium constant of each defect reaction. The equilibrium constants that give the best results are shown in Table 3. Figs. 1 and 2 show the comparison between the calculated results and the experimental values at 1273 and 1573 K, respectively. The empirical fit to 1273 K data looks quite good, while the results of 1573 K fit shows discrepancy near a stoichiomet-

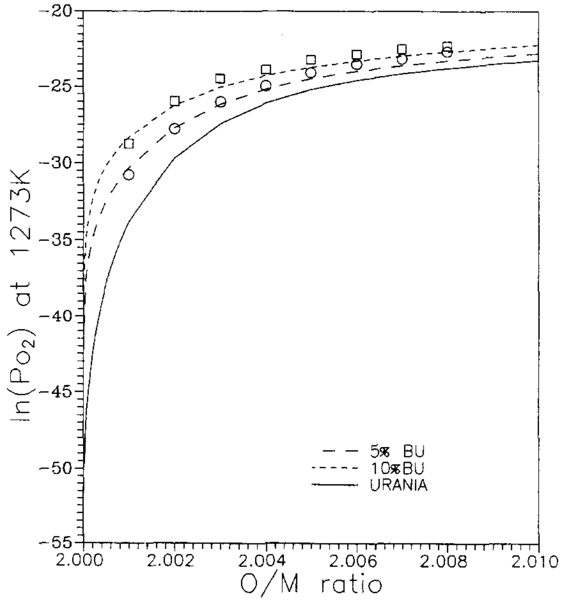

Fig. 1. Comparison between experimental data and calculation values from the model (1273 K).

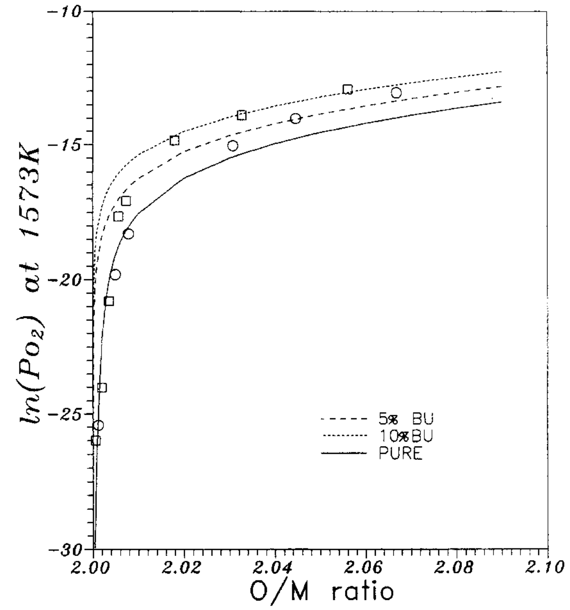

Fig. 2. Comparison between experimental data and calculation values from the model (1573 K).

ric region. Deviations of experimental data of oxygen potential are frequently observed especially near the stoichiometric region [13], and the fitting is emphasized on data of the nonstoichiometric region. This model reasonably explains the behavior of the oxygen potential of the urania fuel with fp's.

## 3. Oxygen potential of urania fuels during irradiation

During irradiation in the reactor, the stoichiometry and the oxygen potential of urania fuel change due to the appearance of fp's. Fission of a U (or Pu) atom generates two fission products and liberates two oxygens. Some of the liberated oxygens can be recombined to form compounds with fp's, but not all the fp's accept the oxygen. Therefore, there is a possibility of the increase of O/M. To find the stoichiometric change during irradiation, we simplify the chemical behavior of fp's as follows:

(i) Noble gases (Xe, Kr) and volatile elements (Br, I) neither react with oxygen nor affect the oxygen potential of the fuel.

(ii) Cs exists as $Cs_2UO_4$.

(iii) Ba forms oxide precipitates, $BaZrO_3$ with Zr.

(iv) Mo exists as metal when the oxygen potential of fuel is lower than the formation free energy of $MoO_2$. Mo is oxidized and stays in the fuel matrix when the fuel oxygen potential is higher. The atomic fraction of Mo in the fuel matrix is $f_{\mathrm{Mo}}$.

(v) The inside oxidation of the cladding is neglected and the fuel solid solution and fp's are chemically equilibrated.

The concentration of an element $i$ produced by the fission is given by

$$N_i = \beta Y_i N_{\mathrm{U}}^0, \tag{5}$$

where $\beta$ is the burn-up, $Y_i$ is the fission yield of $i$ and $N_{\mathrm{U}}^0$ is the initial uranium concentration.

The O/M change due to the fission products is [14]

$$\mathrm{O/M} = [(\mathrm{O/M})_0 - \beta(3Y_{\mathrm{Ba}} + 2Y_{\mathrm{Cs}})]/[(1-\beta) + \beta(Y_{\mathrm{Ln}} + Y_{\mathrm{Pu}} + Y_{\mathrm{Zr}} - Y_{\mathrm{Ba}} + f_{\mathrm{Mo}}Y_{\mathrm{Mo}} - Y_{\mathrm{Cs}}/2)], \tag{6}$$

where $(\mathrm{O/M})_0$ is the initial value of O/M, and the notation for each group is given in Table 1.

Mo in both the fuel matrix and metallics are in equilibrium with each other, and this Mo equilibrium reduces to the following relation:

$$\Delta G_{\mathrm{Mo}}^{\circ} = \overline{\Delta G_{\mathrm{O}_2}} - RT \ln\left(\left(\frac{f_{\mathrm{Mo}}}{1-f_{\mathrm{Mo}}}\right)\frac{\gamma_{\mathrm{f}}}{\gamma_{\mathrm{m}}} \times \frac{\beta(Y_{\mathrm{M}} + (1-f_{\mathrm{Mo}})Y_{\mathrm{Mo}})}{(1-\beta) + \beta(Y_{\mathrm{Ln}} + f_{\mathrm{Mo}}Y_{\mathrm{Mo}} + Y_{\mathrm{Zr}} - Y_{\mathrm{Ba}})}\right), \tag{7}$$

where $\Delta G_{\mathrm{Mo}}^{\circ}$ is the standard formation free energy of $MoO_2$ and $\overline{\Delta G_{\mathrm{O}_2}}$ is the oxygen potential of the fuel. $\gamma_{\mathrm{f}}$ and $\gamma_{\mathrm{m}}$ are the activity coefficients of Mo in the fuel matrix and metallics, respectively.

If the value of initial O/M and the ratio of the activity coefficients of Mo in fuel matrix to that of metallics are known, the oxygen potential change of the fuel during irradiation can be calculated. Fig. 3 shows the change of the oxygen potential of irradiated urania fuels at 750°C considering the equilibrium of Mo between fuel matrix and metallics. In this calculation, the initial O/M is set as 2 and the ratio of the activity coefficients ($\gamma_{\mathrm{f}}/\gamma_{\mathrm{m}}$) as 1. Measured values of the oxygen potential of irradiated fuels [8–10] are compared with the calculated results. Even though we simplified the behaviors of fp's in the fuel, the calculated results explain the measured values reasonably well. The oxygen potential changes slowly as the fuel burns up. Fig. 4 shows the fraction of Mo staying in fuel matrix. Liberated oxygens are consumed by Mo, and the fraction of Mo in the oxide increases with burn-up. Matzke has measured the oxygen potential at the rim region in high burn-up fuels recently [11]. The burn-up range of the rim region is more than 12% and the oxygen potential in that region is measured to be −410 to −450 kJ/mol. Considering the consumption of oxygen due to the inner side oxidation of the cladding, the measured oxygen potential may be lower than the calculated values, where the consumption was neglected. Current models indicate quite similar values as Matzke has measured.

Due to the buffering role of Mo, the oxygen potential changes slowly and so does the stoichiometry. In the calculation shown in Fig. 3, the O/M values change from

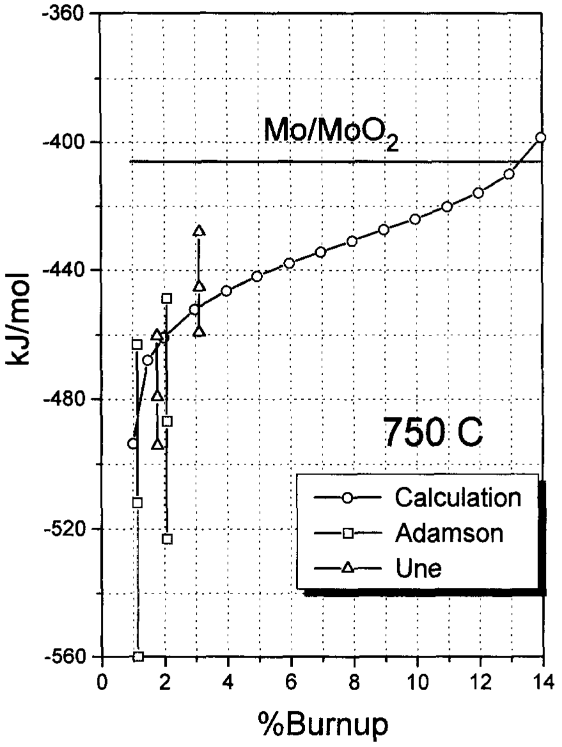

Fig. 3. Oxygen potential change of urania fuel with burn-up.

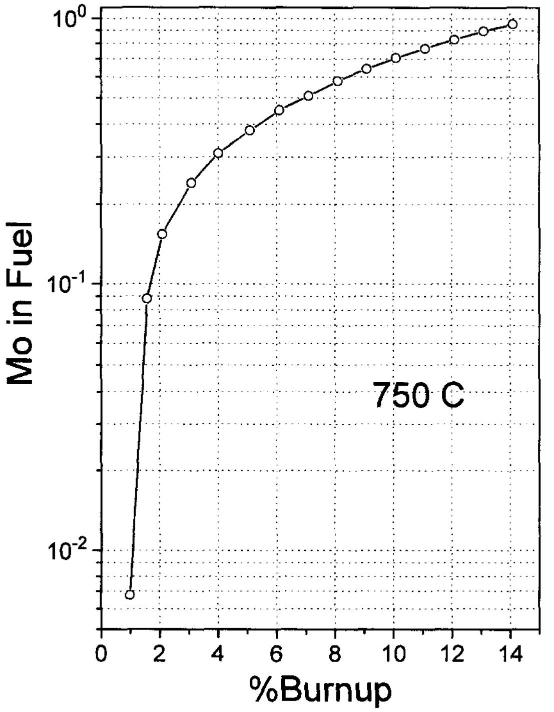

Fig. 4. The fraction of Mo in fuel matrix.

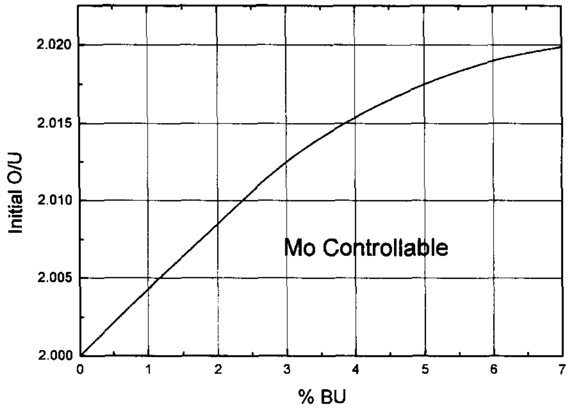

Fig. 5. Mo control line. Mo can control the stoichiometry of fuel if O/U value is under the line.

2.000005 to 2.00001. Eq. (6) gives the O/M limits of fresh urania fuel where the stoichiometry of the fuel can be fully controlled by Mo. Fig. 5 shows the limit of PWR urania fuel. When the initial O/M value is less than the limit, the excess oxygen produced by fission can be consumed by Mo and the fuel behavior is stable due to the negligible change of fuel stoichiometry. In the other case (beyond the limit), the fuel is always in the hyperstoichiometric region and harmful effects may start to show up.

So far, the fuel pellet was assumed to be an isolated system, and the increase of oxygen potential due to liberated oxygens by fission was considered to be controlled by oxygen consumption of metallic Mo. Recent work indicates the possibility of low solubility of $MoO_2$ in urania [16] and the formation of Cs–Mo–O compounds near gaps. A thermodynamic study shows possible formation of $Cs_2MoO_4$ [15]. These Cs–Mo–O compounds makes the analysis of the oxygen potential of irradiated fuel more complex, however, the role of Mo as an oxygen consumer does not change even in Cs–Mo–O compounds. Zircaloy cladding also uptakes oxygen. In the case of 8.3 mm diameter pellet fuel, 1 μm oxide-layer formation on the inner side of cladding changes O/U value by as high as $1 \times 10^{-3}$. So, considering all these possible reactions, measured oxygen potentials of irradiated fuels can be lower than the one from the current model, as in the case of those that Matzke has measured [11].

## 4. Conclusion

Based on the defect structure of pure urania and those of doped urania, a defect model for the irradiated urania fuel is developed. This model reasonably well explains available experimental data.

Using the developed defect model of irradiated urania fuel, the oxygen potential and the stoichiometry of fuel solid solution are traced with burn-up. The oxygen potential of urania fuel changes slowly with burn-up due to the buffering role of Mo. Even in high burn-up, the fuel has the low values of oxygen potential, as observed in Matzke's experiment.

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