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# The Oxygen Potential of Urania Nuclear Fuel During Irradiation

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A defect model for $UO_2$ fuel containing soluble fission products was devised based on the defect structure of pure and doped uranias. Using the equilibrium between fuel solid-solution and fission-products and the material balance within the fuel, a tracing method to get the stoichiometry change of urania fuel with burnup was made. This tracing method was applied to high burnup urania fuel and DUPIC fuel. The oxygen potential of urania fuel turned out to increase slightly with burnup. The stoichiometry change was calculated to be negligible due to the buffering role of Mo. The oxygen potential of DUPIC fuel turned out to be sensitive to the initial chemical state of Mo in the fuel

***Key words :*** Nuclear Fuel, Oxygen potential, Irradiation, DUPIC Fuel, Stoichiometry

## I. Introduction

Nuclear fuel is the energy source for nuclear power plants, and safe and economic operations of nuclear power plants need a good performance of nuclear fuel. Urania ($UO_2$) is a major form of nuclear fuel, nowadays. Oxide fuels are favorable due to their endurable properties at high temperature under the radiation environment. Urania has a broad range of non-stoichiometry at high temperatures. The performance of nuclear fuel depends on the stoichiometry of the fuel. For example, the stoichiometry change of urania fuel directly affects the diffusion coefficient of fission gases and also the thermal conductivity of the fuel matrix.[1,2] The stoichiometry of urania fuel changes during irradiation mainly due to the appearance of fission products (FP's). While the oxygen potential of the fuel is known to determine the chemical states of FP's, the oxygen potential of the fuel is also influenced by the soluble FP's to the fuel matrix

Extended burnup of nuclear fuel is preferred due to the improved economy of nuclear power plant operation. Nuclear fuel contains higher amounts of FP's in this case, and these FP's affect the oxygen potential of the fuel and also the performance. So, the oxygen potential change of high burnup fuel becomes an important issue. In this paper, defect models for pure and doped uranias are reviewed and 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 the fuel at extended burnup and DUPIC fuel.

## II. Fission Product Chemical States.

Kleykamp classified fission products into four groups based on their chemical states in the fuel - volatile FP's, metallic and ceramic precipitates, and oxides dissolved in the fuel.[3] In this study, we divided fission products into 7 groups. Table 1 illustrates the chemical states of FP's in each group. 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

**Table 1.** Elements and Chemical State of Each Group of Fission Products

| Elements | Chemical States | Notation | Fission Yield (%) |
|---|---|---|---|
| Xe, Kr | Noble Gas | Xe | 30.1 |
| Br, I | Volatile | Br | 1.4 |
| Rb, Cs | Cs-U-O, Cs-Mo-O | Cs | 16.7 |
| Mo, Pd. Ru, Rh, Tc | Metal (Mo can be oxide) | M | 58.2 |
| Ag, Cd, In, Sn, Sb | Metal (low melting temp.) | Cd | 2.1 |
| Ba | Oxid Precipitates | Ba | 14.3 |
| Nd, La, Y, Nd, Sm, Eu, Gd Pm, Zr, Ce, Pr | Soluble to Fuel Matrix | Ln | 76.7 |

complicated compounds with U, Mo and O. Mo, Tc, Ru, Rh and Pd are main metallic elements. Mo can be oxide or metallic phases depending on the oxygen potential of fuel. The solubility of $MoO_2$ in urania is known to be small.[4] Ag, Cd, In, Sn, Sb and Te also exist as metallic, but their low vapor pressures make them observed in the vicinity of pores and gap between pellets and cladding. Nd, La, Y, Nd, Sm, Eu, Gd, Pm, Zr, Ce, and Pr form solid solution with $UO_2$ fuel.

The solubility of $ZrO_2$ depends on the fuel temperature. At the temperature below 1200C, the solubility is not high, but when mixed with rare earth elements, the solubility increases. The fission yield of each elemental group is obtained from the calculation of ORIGEN-2.[5] The fission yield of each group in table 1 is based on the 4% burnup. The most produced element in solid FP's is Mo (fission yield=23.4%).

## III. Defect Modeling for the Oxygen Potential of Urania Fuel

Extensive thermochemical studies of the urania fuel have been performed for several decades. The basic structural defects in $UO_2$ are known to be the anion Frenkel pair (oxygen interstitial and oxygen vacancy). The cation Frenkel defects pair is negligible since its formation energy(>12 eV) is much higher than that of the anion Frenkel pair(3-4 eV). Experimental observation indicates the slope of $(\ln Po_2/\ln x)$ in the small x region of $UO_{2+x}$ is 6,[6-8] giving the interstitial an effective charge of -2. At high temperatures, the thermal electronic excitation process is believed to be disproportionation of two $U^{4+}$ ions into one $U^{3+}$ and one $U^{5+}$ ion.[9] Hyland made a simple defect model considering these intrinsic defects, to get the most reliable value of the oxygen potential at the exact stoichiometric $UO_2$.[10]

Willis observed the structure of $UO_{2.12}$ using neutron-diffraction measurements.[11,12] Oxygen ions in this hyperstoichiometric urania turned out to be arranged in a configuration called (2:2:2). In this large x region of $UO_{2+x}$, the slope of $(\ln Po_2/\ln x)$ becomes approximately 2. Nakamura and Fujino introduced clusters in their defect model in hyperstoichiometric region to explain this behavior.[13] Recently, Park and Olander used (2:2:2) clusters and vacancy dimers in describing the oxygen potential of pure urania, in addition to intrinsic point defects.[14] Park and Olander's model reasonably well explains the experimental data in both hypo- and hyper-stoichiometric urania (applicable range: $|x| < 0.1$).

Dopants in the $UO_2$ matrix changes the oxygen potential. If the valence of dopant in the solid solution is less than 4, the oxygen potential of doped $UO_2$ generally increases (or, vice versa).[15-17] There are many thermochemical and mechanical measurements related to several types of doped $UO_2$. Dopants like Gd, Eu are mixed with a fuel as neutron poison.[18-21] Nd, Zr and Ce are major soluble FP's in urania fuel.[22-25] Nb and Mg are important dopants for coarsening the grain of urania fuel during sintering.[26-28] Park and Olander explained the behaviors of Gd- and Eu- doped $UO_2$ based on the pure urania defect structure.[29] They introduced the oxygen interstitial site reduction factor and the clusters composed of oxygen vacancies and dopants in explaining the change of oxygen potential when these dopants are added.

## IV. Role of Soluble Fission Products on the Oxygen Potential of Urania Fuel

The soluble fission products in urania fuel changes the fuel oxygen potential. Major soluble FP's are rare earth elements which are believed to increase the fuel oxygen potential, since the net valence of these FP's is less than 4. Several models have been devised for the explanation of the oxygen potential of the urania fuel containing soluble FP's. Une and Oguma used the cation valence model in describing the oxygen potential of simulated high burnup fuel.[30] The cation valence model has a limit in the working range of stoichiometry, and does not fit to experimental data at near stoichiometric region. Fujino recently developed a statistics-based model.[31] Fujino assumes intra-cation complexes formed in irradiated $UO_2$ fuel with soluble FP's. Even though it is from a sound statistical base, his model cannot be applicable to exact stoichiometric $UO_2$.

In this study, the oxygen potential of urania fuel with soluble FP's is modeled based on the defect structure of pure urania,[14] which is similar to the method applied to Gd- and Eu-doped uranias by Park and Olander.[29] Since there are so many elements in FP's, grouping of FP's is necessary. Soluble FP's are grouped into three categories - Pu, Ln and Zr groups - depending on their valences in the fuel, as shown in Table 2. The solubility of Pu group elements in urania is very high. In the hypostoichiometric region, most Pu ions are known to be reduced to the valence of +3 to meet the charge neutrality. The solu-

**Table 2.** Grouping of Soluble FP's and Their Valence in Fuel Solid Solution

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

bility of Zr in urania is strongly affected by the temperature and the amount of other rare earth elements mixed with. Generally the solubility increases with temperature. The Oxygen potential of urania doped with zirconia is measured to be slightly lower than that of pure urania.[32] However, the Zr concentration in this measurement may exceed the solubility limit, and the measured values by Aronson may not be credible.[33] 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. The valence of rare earth elements, Nd, La, Sm and Y is believed to be +3. Rare earth elements generally increase the oxygen potential of the fuel solid solution.

Nd is the most produced element among rare earth elements from the fission of uranium. So, a defect model for the oxygen potential of the urania fuel containing FP's is made based on the defect structure of Nd-doped urania.[25] The assumptions used in modeling are as follows;

i) The basic defect structure of pure urania is applicable.[14] And, due to the negative effective charge, cations with valence +3 repels nearby doubly-negatively-charged oxygen interstitials, thereby effectively eliminating a certain number of oxygen interstitial sites. The factor for the anion interstitial site reduction due to the addition of dopants is the same as that of Nd-doped urania.[25]

ii) Pu group elements make an equilibrium with uranium ions;

$$Pu_U^x + U_U^x = Pu_U^{\prime} + U_U^{\cdot} \qquad : K_P \qquad (1)$$

iii) $Ln_U^{\prime}$ forms a vacancy cluster with U positive polarons and oxygen vacancies;

$$V_O^{\cdot\cdot} + 4U_U^x + 2Ln_U^{\prime} + U_U = (5U : V : 2Ln) \qquad : K_I \qquad (2)$$

iv) makes a cluster with oxygen interstitials and U positive polarons;

$$O_i^{\prime\prime} + 2U_U^{\cdot} + Ln_U^{\prime} = (2U : O : Ln)^{\prime} \qquad : K_N \qquad (3)$$

v) partially forms a pair with an U positive polaron;

$$U_U^{\cdot} + Ln_U^{\prime} = (U : Ln) \qquad : K_B \qquad (4)$$

vi) The numbers of the 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 quite rare. Une and Oguma have measured the oxygen potential of simulated urania fuel with respect to non-stoichiometry at 1273 and 1573K.[30] Une and Oguma's results were compared 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. Fig. 1 shows the comparison between the calculation results and the experimental values at 1273K. This model reasonably explains the behavior of the oxygen potential of the urania fuel containing FP's.

**Table 3.** Equilibrium Constants for the Defect Reactions

| Temp(K) | ln $K_B$ | ln $K_P$ | ln $K_I$ | ln $K_N$ |
|---|---|---|---|---|
| 1273 | 9 | -8.4 | 15 | 13 |
| 1573 | 2 | -7.1 | 11 | 11 |

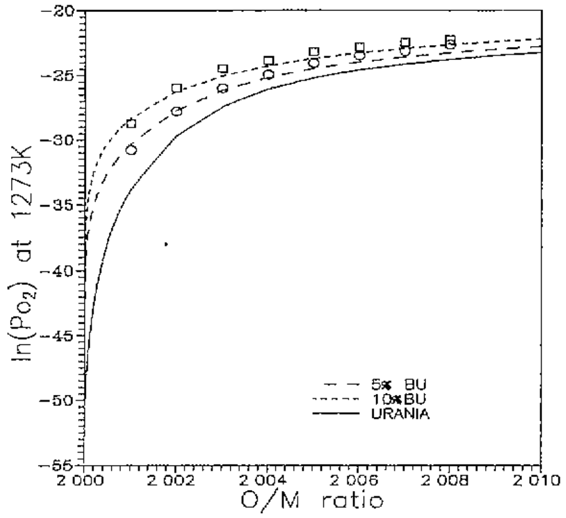

**Fig. 1.** Comparison between experimental data and calculated values from the model (1273K).[30]

# V. The Change of Oxygen Potential of Urania Fuel 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 liberated oxygens can be recombined to form compounds with FP's; but, not all the FP's accept oxygen. Hence, there is a possibility of the increase of O/M. Mo is the most produced solid fission-product element. And the free energy of formation of $MoO_2$ is so close to the oxygen potential of nearly stoichiometric fuel that this fission product cannot be unambiguously assigned to the elemental or the oxide chemical state. So, it is distributed between the oxide and the metallic inclusions in concentration satisfying chemical equilibrium. And, the fuel is a kind of close system where oxygen balance has to be met. To find the stoichiometry and oxygen potential change of urania fuel during irradiation, a tracing model considering both the material balance and the equilibrium in the system was made. In the model, we simplify the chemical behaviors 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 $Cs_2UO_4$.[34]

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 when the fuel oxygen potential is higher. The atomic fraction of Mo in fuel is $f_{Mo}$.

v) The inner side oxidation of the cladding is neglected.

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

$$N_i = \beta Y_i N_U^o \tag{5}$$

where β is burnup, $Y_i$ is fission yield of i, and $N_U^o$ is the initial uranium concentration.

O/M change due to the fission products is ;

$$\left(\frac{O}{M}\right)=\frac{(\frac{O}{M})_O-\beta(3Y_{Ba}+2Y_{Cs})}{(1-\beta)\beta(Y_{Ln}+Y_{Pu}+Y_{Zr}-Y_{Ba}+f_{Mo}Y_{Mo}-Y_{Cs}/2)} \tag{6}$$

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

Mo in both fuel and metallics are equilibrated to each other, and this Mo equilibrium reduces to the following relation.

$$\Delta G_{Mo}^o=\overline{\Delta G}_{O_2}-RT\times$$

$$\ln\left\{\left(\frac{f_{Mo}}{1-f_{Mo}}\right)\frac{\gamma_f}{\gamma_m}\frac{\beta(Y_m+(1-f_{Mo})Y_{Mo})}{(1-\beta)+\beta(Y_{Ln}+f_{Mo}Y_{Mo}+Y_{Zr}-Y_{Ba})}\right\} \tag{7}$$

where $\Delta G_{Mo}^o$ is the standard formation free energy of $MoO_2$ and $\overline{\Delta G}_{O_2}$ is the oxygen potential of fuel. $\gamma_f$ and $\gamma_m$ are the activity coefficients of Mo in fuel and metallics, respectively.

If the value of initial O/M and the ratio of activity coefficients of Mo in fuel to that of metallics are known, the oxygen potential change of fuels during irradiation can be calculated. Fig. 2 shows the oxygen potential change of irradiated urania fuels at 750C using this tracing method. In this calculation, the initial O/M is set as 2 and the ratio of activity coefficients ($\gamma_f/\gamma_m$) as 1. Measured values of the oxygen potential of irradiated fuels[35,36] are compared with the calculation results. Even though we simplified the behaviors of FP's in the fuel, the calculation results explain the measured values reasonably well. The oxygen potential changes slowly as the fuel burns up. The main reason for this behavior is due to the buffering role of Mo. Liberated oxygens are consumed by Mo, increasing the fraction of Mo in the oxide with burnup. Matzke has measured the oxygen potential of the rim region in high burnup fuels, recently.[37] The burnup range of the rim region corresponds to more than 12%, and the oxygen potential in that region was measured to be -410 to -450 kJ/mol. Considering the consumption of oxygen due to inner side oxidation of cladding, the measured oxygen potential may be lower than the calculation values where the consumption was neglected. Current model indicates 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 case of the calculation shown in Fig. 2, the O/M values change from 2.000005 to 2.00001. Equation (6) gives the O/M limit of fresh urania fuel where the stoichiometry of fuel can be fully controlled by Mo. Fig. 3 shows this limit of PWR urania fuel. When the initial O/M value is less than the limit, the excess oxygens 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 (over 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 oxygen by fission was considered to be controlled

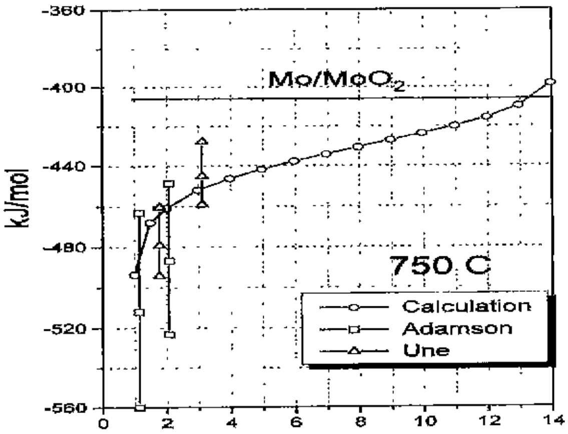

**Fig. 2.** Oxygen potential change of urania fuel with burnup.

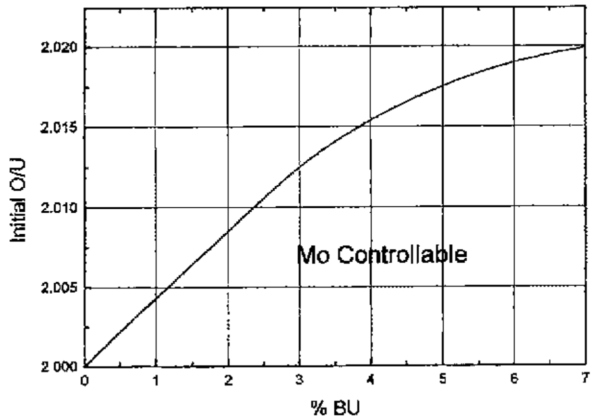

**Fig. 3.** Mo control line. Mo can control the stoichiometry of fuel if O/U value is under the line.

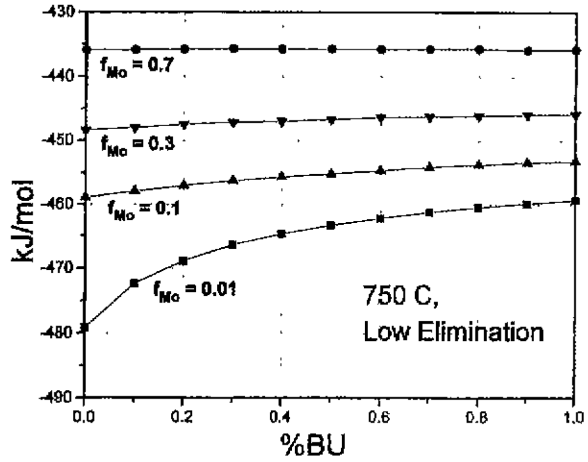

**Fig. 4.** Oxygen potential of DUPIC fuel during irradiation, The temperature is 750 C. $f_{MO}$ is oxide fraction.

only by the oxygen consumption by metallic Mo. Recent works indicate the possibility of low solubility of $MoO_2$ in urania[4] and the formation of Cs-Mo-O compounds near gap. Thermodynamic study shows possible formation of $Cs_2MoO_4$.[34] These Cs-Mo-O compounds make 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. Kleykamp insists cladding inner-side oxidation is a dominant process for the oxygen potential change during irradiation. So, considering all these possible reactions, measured oxygen potential of irradiated fuel can be lower than the one from the current model, as in the case of those that Matzke has measured.[37]

The tracing method developed in this study can be applicable to DUPIC (Direct Use of spent PWR fuel In CANDU) fuel. Since DUPIC fuel is made from resintering of powdered spent PWR fuel, DUPIC fuel already contains lots of FP's initially. The composition of DUPIC fuel is dependent on the extent of PWR fuel burnup and the Dry process, i.e., a process where spent PWR fuel is powdered and resintered. Many volatile FP's are expected to be eliminated from the fuel during the Dry process. Since the Dry process is still under development, the composition of DUPIC fuel is not known yet. In this study, we assumed the low elimination of FP's, where Mo fully survives during the Dry process and stays in DUPIC fuel. The calculation results are shown in Fig. 4. The O/M value of DUPIC fuel before irradiation is assumed as 2 and the spent PWR fuel is burned up to 35, 000 MWD/MTU in the calculation. In the figure, $f_{Mo}$ indicates the fraction of $MoO_2$ in total molybdenum in DUPIC fuel. Since only metallic molybdenum works for the buffering role consuming liberated oxygen, the oxygen potential of DUPIC fuel increases as the oxide fraction in Mo ($f_{Mo}$) in the fuel increases. Hence, the control of stoichiometry and that of Mo chemical states during the production of the DUPIC fuel seem to be important for the better quality of the fuel.

## VI. Conclusion

Based on the defect structure of pure urania and those of doped uranias, a defect model for the oxygen potential of the urania fuel containing soluble FP's is developed. This model reasonably well explains available experimental data. Using this developed defect model, a tracing method to find the oxygen potential and the stoichiometry change of urania fuel during irradiation is made. The tracing method is applied to high burnup urania fuel and DUPIC fuel. The oxygen potential of urania fuel changes slowly with burnup due to the buffering role of Mo. Even in high burnup, the fuel has the low values of oxygen potential, as observed in Matzke's experiment. The oxygen potential of DUPIC fuel strongly depends on the chemical states of Mo. For the better quality of the fuel, the control of stoichiometry and that of Mo chemical states during the production of the DUPIC fuel become important.

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