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 among fuel solid-solution and fission-products and the material balance within the fuel, the stoichiometry change of the urania fuel was traced with burnup. This tracing method was applied to high burnup fuels and DUPIC, and the implications were discussed.

I. INTRODUCTION

The stoichiometry of the urania fuel has strong effects on the performance of nuclear fuels. With the increase of hyperstoichiometry, the diffusion coefficient of fission gases increases[1] and the thermal conductivity of the fuel matrix decreases[2]. This trend is harmful because they are interrelated and seem to accelerate each other. The fuel stoichiometry may change during irradiation due to the appearance of fission product (F.P's). The oxygen potential of the fuel determines the chemical states of F.P's. However, the oxygen potential of the fuel is also influenced by the soluble F.P's to the fuel matrix.

Economical uses of nuclear fuels make a trend for the extended burnup, nowadays. High burnup fuels contain lots of F.P's, and these F.P's affect the stoichiometry of the fuels and also the performance. So, the stoichiometry change of high burnup fuels becomes one of concerns. DUPIC(Direct Use of spent PWR fuels Into CANDU) fuels, which decrease the amount of radioactive wastes per electricity generated, are being developed. DUPIC fuels already contain lots of F.P's initially. And the effects of F.P's has to be analyzed in detail.

II. OXYGEN POTENTIAL OF IRRADIATED FUELS

1. Chemical State of Fission Products

Table 1 illustrates the chemical states of F.P's in groups in urania fuels. 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 metallic. Ag, Cd, In, Sn, Sb and Te also exist as metallics, 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, and Pr form the solid solution with UO_2 fuel.

2. The Oxygen Potential of Urania Fuels containing Soluble Fission Products.

The oxygen potential of the urania fuel with soluble F.P's is modeled based on the defect structure of pure urania[3]. Since F.P's are composed of many kinds of elements, grouping of F.P's is necessary. We divide the soluble F.P's into three groups - Pu, Ln and Zr groups - depending on their valences in the fuel, as shown in Table 2. Pu, an actinide is included since Pu also affects the oxygen potential of urania fuels. Pu, Ce are very soluble to urania, and easy to be reduced comparing to U under the reducing condition. 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 the addition of Zr in it[4]. However, the Zr concentration in this measurement may exceed the solubility limit, and the measured values by Aronson may not be credible[5]. Hence, we assume that Zr does not give any effects 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 F.P's is made based on the defect structures of doped uranias[6,7]. The model assumptions are 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;

$$\mathrm{Pu_U^x + U_U^x = Pu_U^{/} + U_U^{\bullet}} \qquad : \ \mathrm{K_P} \qquad (1)$$

iv) $Ln_U^{/}$ forms a vacancy cluster with U positive polarons and oxygen vacancies;

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

v) $Ln_U^{/}$ makes a cluster with oxygen interstitials and U positive polarons and oxygen interstitials;

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

vi) $Ln_U^{/}$ partially forms a pair with an U positive polaron;

$$U_U^{\bullet} + Ln_U' = (U{:}Ln) \qquad : \; K_B \qquad (4)$$

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 fuels with respect to non-stoichiometry at 1273 and 1573K using a Gravimetric method[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. Figure 1 and 2 show the comparison between the calculation results and the experimental values at 1273 and 1573K, respectively. This model reasonably well explains the behavior of the oxygen potential of the urania fuel with F.P's.

III. OXYGEN POTENTIAL OF URANIA FUELS DURING IRRADIATION

During irradiation in the reactor, the stoichiometry and the oxygen potential of urania fuels change due to the appearance of F.P'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 F.P's; but, not all the F.P's accept oxygen. So, there is a possibility of the increase of O/M. To find the stoichiometry change during irradiation, we simplify the chemical behaviors of F.P'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 fuel matrix when the fuel oxygen potential is higher. The atomic fraction of Mo in fuel matrix is f_{Mo}.
v) The inner side oxidation of the cladding is neglected. And, the fuel solid solution and F.P's are chemically equilibrated.

1. Application to High Burnup Fuels

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

$$N_i = \beta Y_i N_U^{\circ} \qquad (5)$$

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

O/M change due to the fission products is ;

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

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

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

$$\Delta G^{\circ}_{Mo} = \overline{\Delta G}_{O_2} - RT\ln\left(\left(\frac{f_{Mo}}{1-f_{Mo}}\right)\frac{\gamma_f}{\gamma_m}\frac{\beta(Y_M + (1-f_{Mo})Y_{Mo})}{(1-\beta)+\beta(Y_{Ln} + f_{Mo}Y_{Mo} + Y_{Zr} - Y_{Ba})}\right) \qquad (7)$$

where ΔG°_{Mo} is the standard formation free energy of MoO_2 and $\overline{\Delta G}_{O_2}$ is the oxygen potential of fuel. γ_f and γ_m are the activity coefficients of Mo in fuel matrix and metallics, respectively.

If the value of initial O/M and the ratio of activity coefficients of Mo in fuel matrix to that of metallics are known, the oxygen potential change of fuels during irradiation can be calculated. Figure 3 shows the oxygen potential change of irradiated urania fuels at 750C° considering the equilibrium of Mo in both fuel matrix and metallics. In this calculation, the initial O/M is set as 2 and the ratio of activity coefficients (γ_f/γ_m) as 1. Measured values of the oxygen potential of irradiated fuels[8,9] are compared with the calculation results. Even though we simplified the behaviors of F.P's in the fuel, the calculation results explain the measured values reasonably well. The oxygen potential changes slowly as the fuel burns up. Figure 4 shows the fraction of Mo staying in fuel matrix. Liberated oxygens are consumed by Mo, and the fraction of Mo in fuel matrix increases with burnup. Matzke has measured the oxygen potential of the rim region in high burnup fuels, recently[11]. The burnup range of the rim region corresponds to 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 inner side oxidation of cladding, the measured oxygen potential may be lower than the calculation values where the consumption was neglected. So, 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 Figure 3, 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 can be fully controlled by Mo. Figure 5 shows the limit of PWR fuels. 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 degree of non-stoichiometry. In the other case (over the limit), the fuel is always in the hyperstoichiometric region with high degree of non-stoichiometry, and harmful effects may start to show up.

2. Application To DUPIC Fuels

DUPIC fuels are made from spent PWR fuels by Dry Process. The compositions of DUPIC fuels are dependent on the extent of PWR fuel bunrup and the procedures during Dry Process. Since Dry Process for the production of DUPIC fuels is still under development, the composition of F.P's in DUPIC fuels is not known yet. We set 2 scenarios to see the behavior of DUPIC fuels -- low and high elimination of F.P's during Dry Process. Table 3 shows the assumed elemental elimination models (or scenarios) during Dry Process. After Dry Process, Mo fully survives and stays in fuel in the case of low elimination, while 1% of Mo survives in the other case.

O/M change of DUPIC fuels during irradiation is given by;

$$\left(\frac{O}{M}\right)=\frac{\left(\frac{O}{M}\right)_O (N_T^o+f_{Mo}^o N_{Mo}^o)-3(N_{Ba}-N_{Ba}^o)-2(N_{Cs}-N_{Cs}^o)-2(f_{Mo}N_{Mo}-f_{Mo}^o N_{Mo}^o)}{N_T+f_{Mo}N_{Mo}} \qquad (8)$$

where, $N_T = N_U + N_{Pu} + N_{Ln} + N_{Ce} + N_{Zr} - N_{Ba} - \frac{N_{Cs}}{2}$ and superscript, o indicates the initial value.

The equilibrium of Mo between fuel matrix and metallics gives the following relation.

$$\Delta G_{Mo}^{o} = \overline{\Delta G}_{O_2} - RT\ln\left(\left(\frac{f_{Mo}}{1-f_{Mo}}\right)\frac{\gamma_f}{\gamma_m}\frac{(N_M+(1-f_{Mo})N_{Mo})}{N_T}\right) \qquad (9)$$

The concentration of each element in DUPIC fuels during burnup is calculated by ORIGEN-2[12] using CANDUSEU library. Figure 6 and 7 show the results of calculation in the case of low and high elimination, respectively. The O/M value of initial DUPIC fuel is set as 2 in the calculation. It should be emphasized that Mo working for buffering during irradiation is only that in metallics. The effect of the chemical state of Mo on the fuel oxygen potential is shown in Figure 6 in the low elimination case. As the fraction of Mo staying in fuel matrix increases, the buffering ability of Mo is reduced to increase fuel oxygen potential. The buffering role of Mo is also observable in the high elimination case(Figure 7); but available Mo is exhausted and similar oxygen potential behaviors are expected after a certain burnup regardless of the initial state of Mo.

The range of O/M values of DUPIC fuel is narrow - 2.00001 to 2.00008 - in this calculation. The control limits of Mo on O/M values of initial DUPIC fuel appear on Figure 8 with respect to the Dry Process procedure and Mo chemical states. When Mo exists as oxide in fuel matrix, the buffering role no longer exists, especially at low burnup. So, the control of stoichiometry and that of Mo chemical states during the production seem to be important for the better quality of DUPIC fuel.

IV. CONCLUSION

1. Based on the defect structure of pure urania and those of doped uranias, a defect model for the irradiated urania fuel is developed. This model reasonably well explains available experimental data.
2. Using the developed defect model of irradiated urania fuel, the oxygen potential and the stoichiometry of fuel solid solution are traced with burnup. The oxygen potentials of urania fuels change 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.
3. The oxygen potential of DUPIC fuel during irradiation depends on the procedure of Dry Process and the chemical states of Mo. Only Mo in metallics does a buffering role in fuel. The stoichiometry of fuel changes very slowly during burnup. But, the initial chemical state and the amount of Mo can change the oxygen potential noticeably. So the stoichiometry of fresh DUPIC fuel and the chemical state of Mo should be adequately controlled for the better quality of DUPIC fuel.

ACKNOWLEDGMENT

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Elements	Chemical States	Notation
Xe, Kr	Noble Gas	Xe
Br, I	Volatiles	Br
Rb, Cs	Reactive. Cs-U-O, Cs-Mo-O	Cs
Mo, Tc, Ru, Rh, Tc	Metal. Mo can be oxide	M
Ag, Cd, In, Sn, Sb	Metal. Low T_M	Cd
Ba	Oxide Precipitates	Ba
Nd,La,Y, Nd,Sm, Eu, Gd Pm, Zr, Ce, Pr	Soluble to Fuel Matrix	Ln

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

Element	Valence	Characteristics
Pu, Ce, Pr	+3, +4	Mainly +4, +3 in reducing codition.
Nd,La,Y, Nb,Sm,Eu,Gd,Pm	+3	always +3
Zr, Mo	+4	always +4

Table 2. Grouping of soluble F.P's and their valence in fuel solid solution.

Elements	Elimination during Dry Process(%)	
	High Elimination	Low Elimination
Xe, Kr, Rn	100	95
Br, I	100	95
Cs, Rb	99	90
Mo	99	0
Rh	100	40
Ru	100	10
Pd	30	0

Table 3. Two scenarios of elemental elimination during Dry Process.

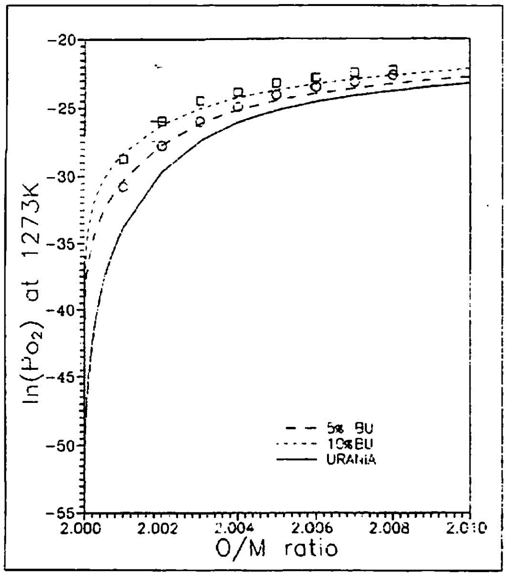

Figure 1. The comparison between experimental data and calculation values using a defect model (1273K).

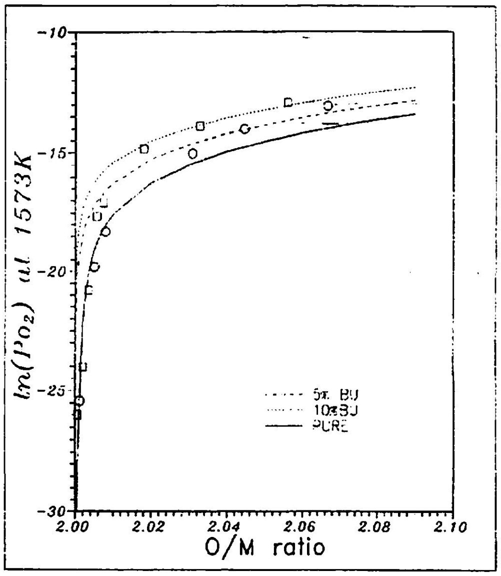

Figure 2. The comparison between experimental data and calculation values using a defect model(1573K).

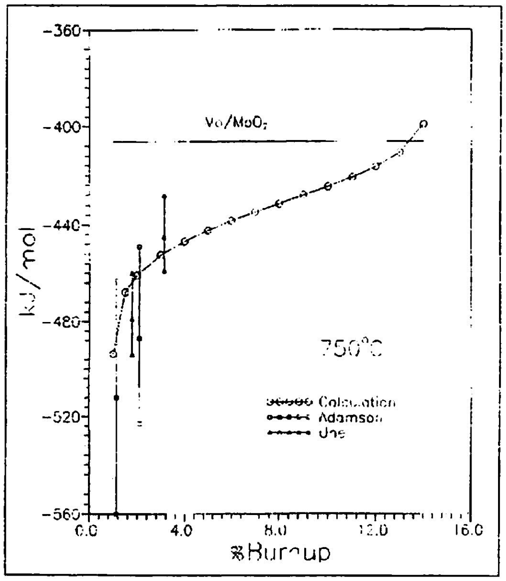

Figure 3. Oxygen potential change of urania fuel during irradiation.

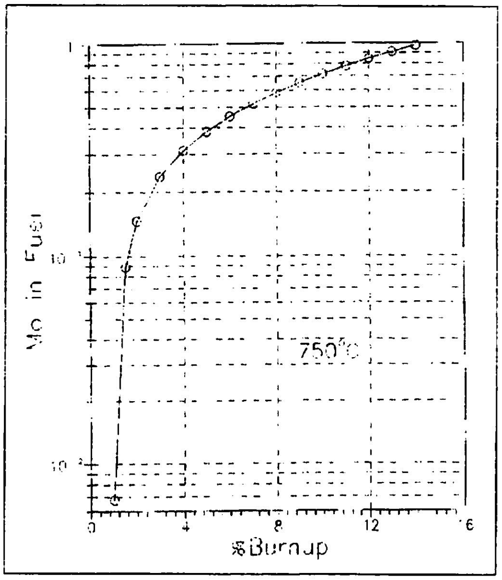

Figure 4. The fraction of Mo in fuel matrix.

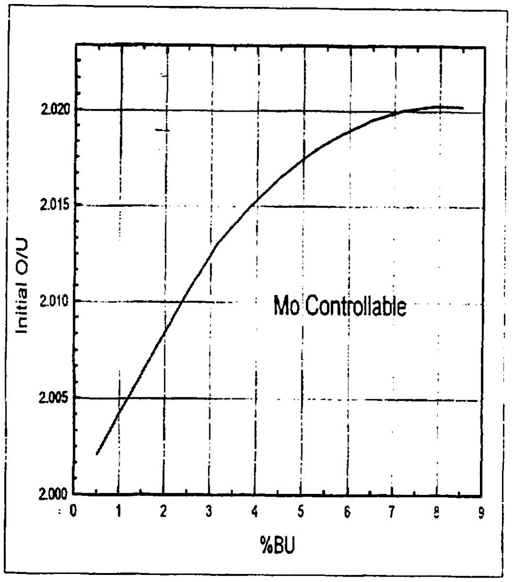

Figure 5. Critical O/U value of urania fuel. Mo can control the stoichiometry of fuel if the O/U value is under the line.

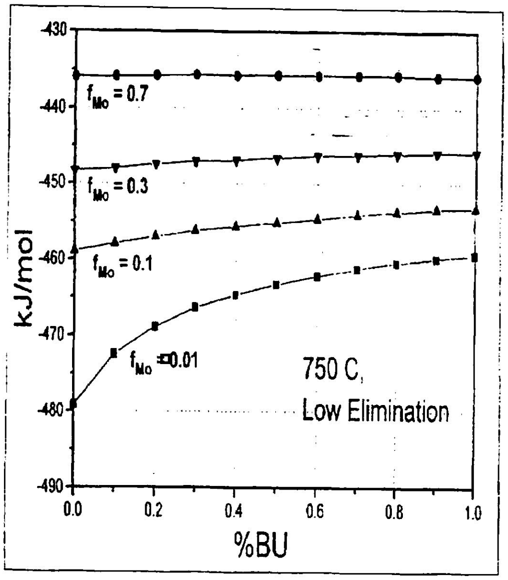

Figure 6. Oxygen potential of DUPIC fuel during irradiation in the low eliminaiton case.

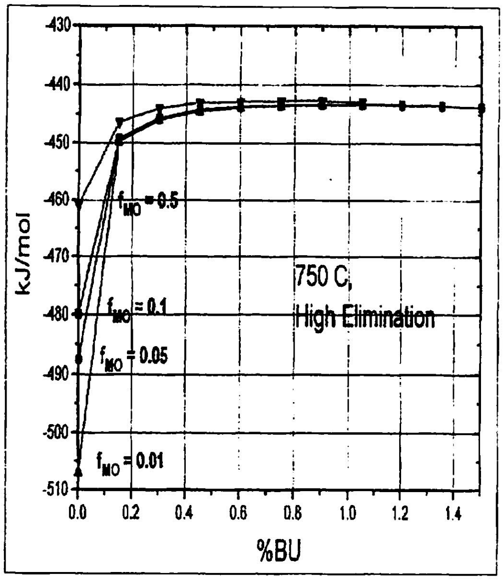

Figure 7. Oxygen potential of DUPIC fuel during irradiation in the high eliminaiton case.

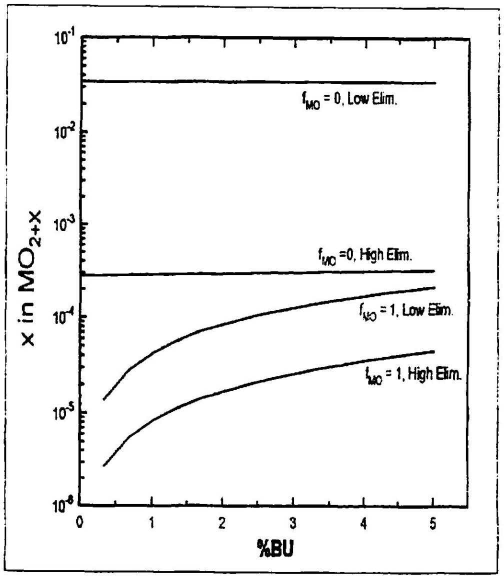

Figure8. Critical initial non-stoichiometry of DUPIC fuel. Critical values depend on Mo chemical states(f_{MO}).