

The oxidation of uranium dioxide in dry storage

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1. Introduction

In dry air storage conditions, the oxidation of the uranium dioxide pellets can be described as a two-step process ($\text{UO}_2 \rightarrow \text{U}_4\text{O}_9/\text{U}_3\text{O}_7 \rightarrow \text{U}_3\text{O}_8$). In the first step, oxygen spreads along the grain boundary and UO_2 is oxidized to $\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$. Formation of $\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$ from UO_2 involves a slight volume reduction. In the second step, the formation of U_3O_8 follows through a nucleation-and-growth mechanism. The density of U_3O_8 is 23% less than that of UO_2 , which corresponds to a 36% net volume increase of oxidized pellets. As a result, the formation of U_3O_8 leads to fuel splitting. In this study, we examine each step of the oxidation process. And the oxidation of spent fuels to U_4O_9 was modeled by COMSOL.

2. Methods and Results

2.1 Oxidation of UO_2 to $\text{U}_3\text{O}_7/\text{U}_4\text{O}_9$

The oxidation of UO_2 begins from the formation of $\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$. Oxygen penetrates through grain boundaries oxidizing UO_2 grains. Thermodynamically UO_2 transforms to U_4O_9 and then U_3O_7 layers with the addition of oxygen. However, Aronson found only U_3O_7 was observed during oxidation of UO_2 powder [1]. In the case of oxidation of pure UO_2 , U_3O_7 phase is thought to appear. The chemical diffusion coefficients of oxygen during oxidation were measured and they are listed below.

Aronson[1] :

$$D = 5.5 \times 10^{-3} \exp\left(\frac{-110460 \pm 6300 \text{ kJ/mol}}{RT}\right) \quad [\text{cm}^2/\text{sec}] \quad (1)$$

Saito[2] :

$$D = 8.33 \times 10^6 \exp\left(\frac{-170401.66 \text{ kJ/mol}}{RT}\right) \quad [\text{cm}^2/\text{sec}] \quad (2)$$

Walker[3] :

$$k = 1.066 \times 10^{-1} \exp\left(\frac{-117260.36 \text{ kJ/mol}}{RT}\right) \quad [\text{cm}^2/\text{sec}] \quad (3)$$

Poulesquen [4] :

$$D_{\text{U}_4\text{O}_9} = 1.16 \times 10^1 \exp\left(\frac{-123000 \text{ kJ/mol}}{RT}\right) \quad [\text{cm}^2/\text{sec}] \quad (4)$$

In the case of oxidation of spent fuels, only U_4O_9 phase was observed. This might be due to the stabilization of cubic structure by soluble fission products. The chemical diffusion coefficients from the oxidation reaction rate constants are listed below.

Woodley[5] :

$$k = 1.4 \times 10^{-4} \exp\left(\frac{-83851.91 \text{ kJ/mol}}{RT}\right) \quad [\text{cm}^2/\text{sec}] \quad (5)$$

Poulesquen [6] :

$$D = 6.68 \times 10^{-6} \exp\left(\frac{-74700 \text{ kJ/mol}}{RT}\right) \quad [\text{cm}^2/\text{sec}] \quad (6)$$

According to the McEachern[7], the relationship between diffusion coefficient(D^0) and oxidation rate constant(k) follows ' $D^0=50k$.'

2.2 Oxidation of U_4O_9 to U_3O_8

The second step of the oxidation of spent nuclear fuels is the oxidation of U_4O_9 to U_3O_8 . Kinetically this oxidation process is known to be controlled by a nucleation-and growth mechanism. By observing the growth of U_3O_8 on UO_2 disk, McEachern[8] made a kinetic model of the nucleation-and-growth mechanism. He assumed that the growth rate of U_3O_8 is only temperature dependent and the 2 dimensional model can be applicable to 3 dimension. He also introduced growth rate, K_g and nucleation rate per unit area, K_n . The transformed fraction of the final phase was found as follows.

$$\alpha(t) = 1 - \exp\left\{-\frac{\pi K_t^3}{3} + \frac{\pi^2 K_t^2 t^6}{180} - \frac{11\pi^3 K_t^3 t^9}{45360} + \frac{5\pi^4 K_t^4 t^{12}}{399168} \dots\right\} \quad (7)$$

where, $K = K_g^2 K_n$.

By examining experimental data of the oxidation of spent fuels, K value was found as [8];

$$\ln K (h^{-3}) = \frac{52808 \pm 3442}{T} + 86.165 \quad (8)$$

2.3. Oxidation modeling

A detail kinetic evaluation of the oxidation of spent fuel pellets needs a modeling of several steps. Oxygen has to penetration through a defect hole (or scratches) to reach fuel pellet surface. Then UO_2 is oxidized to $\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$ by a diffusion mechanism. $\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$ phases have higher density than UO_2 and grain boundary separation occurs resulting in fission gas release. After formation of $\text{U}_4\text{O}_9/\text{U}_3\text{O}_7$ layers, U_3O_8 is nucleated on the early formed surface and grows to expand. Volume expansion by the formation of U_3O_8 layers leads to splitting of spent fuel cladding, which needs stress analysis of cladding. This modeling process can be explained by Figure 1.

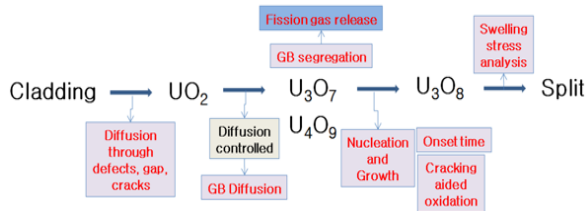


Figure 1. Schematics of modeling of defective fuel oxidation.

One of important parameters in description of fuel pellet oxidation can be a time for U_3O_8 to start to grow. A conservative calculation can be a duration time to reach to U_4O_9 . Einziger[9] and Poulesquen[6] evaluated the duration time to full oxidation to U_4O_9 .

Einziger[9]:

$$t_{24}(h) = 2.6 \times 10^{-9} \exp\left(\frac{111.37 \text{ kJ/mol}}{RT}\right) \quad (9)$$

Poulesquen[6]:

$$t_{admitt}(h) = \frac{1.938 \times 10^{31}}{T(^{\circ}C)^{11.936}} \quad (10)$$

This duration time can be a time for U_3O_8 to start to form in the fuel pellet. And this time can be one at which spent fuel starts to split, conservatively.

2.4 Analysis of spent fuel using COMSOL

Using COMSOL, the first step of changes from UO_2 to U_4O_9 during oxidation process was modeled. The radius of UO_2 particle was assumed to be $6\mu m$. At low temperatures ($<250^{\circ}C$), the x and y value of UO_{2+x} and U_4O_{9+y} were assumed be about 0.001. We solved the diffusion problem of moving boundaries in a sphere simulating fuel pellet grains. The modeling of UO_2 oxidation was schematized as shown in figure 2.

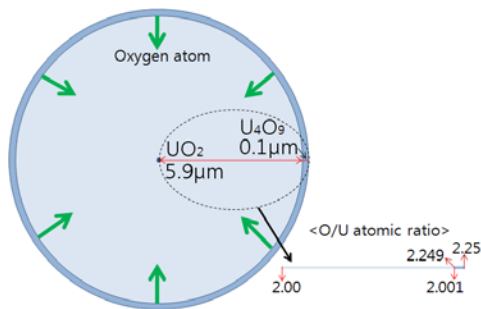


Figure 2. Schematization of oxidation model

The diffusion coefficients of U_4O_9 and UO_2 layers used to solve the moving boundary diffusion problem are as follows.

$$D_{U_4O_9} = 1.36 \times 10^{-6} \exp\left(\frac{-57000}{RT}\right) \text{ [cm}^2/\text{sec]} \quad (11)$$

$$D_{UO_2} = 1.15 \times \exp\left\{\frac{-(56700 \pm 1000) \times 4.2}{RT}\right\} \text{ [cm}^2/\text{sec]} \quad (12)$$

At 523K, radial advancement of interphase layer with respect to oxidation time was calculated and the result was shown in the figure below.

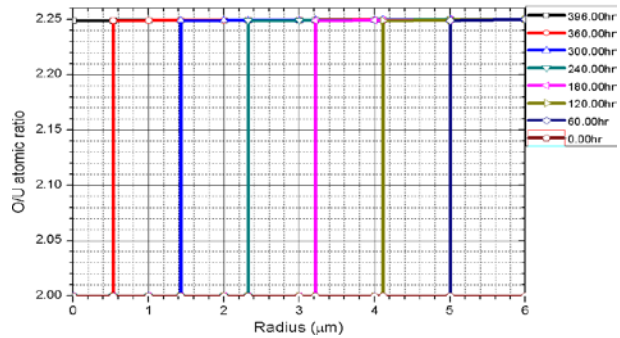


Figure 3. Radial advancement of interphase layer with time during oxidation of a grain of UO_2 at 523K.

3. Conclusions

By observing the oxidation mechanism of spent fuel pellets in the dry storage condition, there are two steps in oxidation- oxidation of fuel pellets to U_4O_9/U_3O_7 (pure UO_2 to U_3O_7 / spent fuel to U_4O_9), and then to U_3O_8 . The oxidation UO_2 to U_4O_9/U_3O_7 is a diffusion controlled mechanism, while the oxidation to U_3O_8 is due to nucleation-and-growth. Based on these oxidation processes, a method of modeling was suggested. One of important time to be evaluated is the splitting time of spent fuel due to oxidation. This time can be the one to reach a full oxidation to U_4O_9 conservatively since U_3O_8 starts to form after the formation of U_4O_9 . The time to full oxidation to U_4O_9 modeled using COMSOL. We solved a moving boundary diffusion problem to get the time to reach to U_4O_9 .

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