

## Experimental analysis of Oxidation and Reduction of Uranium Oxide and formation of Solid Solution of $\text{UO}_2\text{-ZrO}_2$

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### 1. Introduction

A few years ago, there was a huge accident in Fukushima. The nuclear fuel was exposed to the air after accident. the fuel rod melted and dropped to the bottom .  $\text{UO}_2 + \text{ZrO}_2$  solid solution is interested in core melting in NPP. So there has been studying about the compound which is like  $\text{UO}_2 + \text{ZrO}_2$  in Japan. Many scientists have studied about the transition of that compound by heating  $\text{UO}_2 + \text{ZrO}_2$  up.

Additionally Understanding of oxidation and reduction of  $\text{UO}_2$  is very important. During the oxidation and reduction of  $\text{UO}_2$  process phase transition can be occurred. It can cause severe damage in cladding by volume expansion through phase transition. So we have to know about the  $\text{UO}_2$  oxidation and reduction process.

In our study, we conducted two experiment. First, we did experiment which is related about the transition of  $\text{UO}_2$  by heating it up. The process is reduction and oxidation (REDOX). After heat treatment. We used XRD to analyze the structure of material. second we used TG-DTA to analyze weight gain and enthalpy of each reaction.

In second experiment. we did experiment which is related about the Formation of Solid Solution  $\text{Zr}_y\text{U}_{1-y}\text{O}_2$ . Heating up the temperature from R.T to  $1400^\circ\text{C}$  using  $\text{Ar} + 10\% \text{H}_2$  gas. In this experiment, we investigate the morphology of  $\text{Zr}_y\text{U}_{1-y}\text{O}_2$  by scanning electron microscopy (SEM). In addition, the structure change by the formation of solid solution were examined using X-ray diffraction (XRD).

### 2. Methods and Results

#### 2.1 Procedure of $\text{UO}_2$ Oxidation and Reduction

First. We have to make a fine  $\text{UO}_2$  and  $\text{UO}_3$  powder to be oxidation and reduction easily. After making a fine  $\text{UO}_2$  and  $\text{UO}_3$  powder , we should check the exact weight of  $\text{UO}_2$  and  $\text{UO}_3$ . Then, Put the sample on the TG-DTA. TG is measured change of sample weight during the process. In oxidation experiment,  $\text{UO}_2$  powder is heated to  $500^\circ\text{C}$  with  $10^\circ\text{C}/\text{min}$  heating rate. Under air atmospheric condition. In reduction experiment ,  $\text{U}_3\text{O}_8$  powder is heated to  $800^\circ\text{C}$  with  $20^\circ\text{C}/\text{min}$  with heating rate. Under argon atmospheric condition with 10% hydrogen. DTA(Differential thermal analysis) is measured temperature difference between sample and reference. Reference material is  $\text{Al}_2\text{O}_3$  with platinum plate.  $\text{Al}_2\text{O}_3$  is inert material and have a high melting temperature. So  $\text{Al}_2\text{O}_3$  is used reference material in DTA.



Fig 1. TG-DTA

After the oxidation and reduction process, Put the  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  powder on the XRD sample holder. by using XRD, we can analysis the change of the lattice parameter. During the setting the sample on the holder. we have to check the sample height is same with the holder. The error of the height can make the peak shape of the XRD peaks.



Fig 2. XRD

#### 2.2 Procedure of solid solution $\text{Zr}_y\text{U}_{1-y}\text{O}_2$ ( $y = 0.05$ and $0.1$ )

Two sample were prepared with different molar ratio.(  $95\% \text{UO}_2 + 5\% \text{ZrO}_2$ ,  $90\% \text{UO}_2 + 10\% \text{ZrO}_2$ ) And then,  $\text{UO}_2$  and  $\text{ZrO}_2$  powder blended for 20 minutes. after blending, put the sample in the furnace for heat treatment. heat treatment following four step, first, heating up to  $1000^\circ\text{C}$  for 2 hours, And then, heating up to  $1450^\circ\text{C}$  within 2 hour,  $1450^\circ\text{C}$  within 1 hour, cooling down to  $400^\circ\text{C}$ . during the heat treatment, we put the  $\text{Ar} + 10\% \text{H}_2$  with  $20 \text{cc}/\text{min}$  for preventing the oxidation of sample.

After heat treatment, we make a SEM-EDX sample to measure the size of the particle and ratio of U and Zr in the sample.  $\text{UO}_2$  has low conductivity so we need to coating Au, Pd on surface, also we make a XRD sample. by using XRD, we can measure the change of the lattice parameter by ratio of U and Zr.

### 3. Result and discussion

#### 3.1 Result of $UO_2$ Oxidation and $U_3O_8$ Reduction by TG-DTA

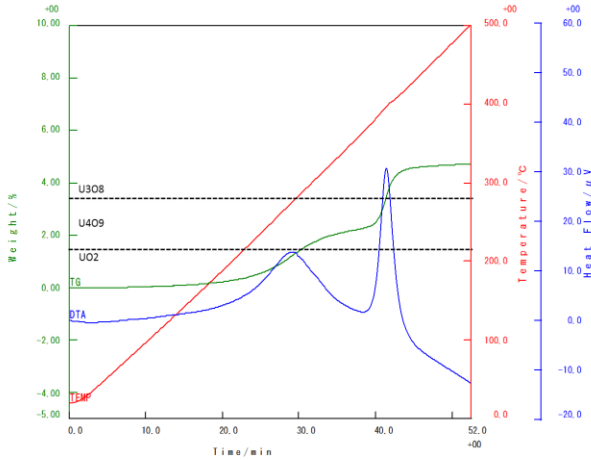


Fig 3. TG-DTA curve of oxidation process

In Fig 3, mass gradient is steeply change around the black line. green line shows the mass change in ratio compare to initial mass. Initial mass of  $UO_2$  was 16.77mg.  $UO_2$  oxidation process has a two mechanism which are to be  $U_4O_9$  and  $U_3O_8$ . Theoretical mass change of  $UO_2$  to  $U_4O_9$  is 1.48wt% and  $U_4O_9$  to  $U_3O_8$  is 3.95wt%, In our experiment, Mass change of  $UO_2$  to  $U_4O_9$  is about 1.48wt%, and mass change of  $U_4O_9$  to  $U_3O_8$  is about 3.79wt%. Thus, our result were in good agreement with theoretical mass change.

DTA line shows two peaks. around the black line. This peak show us its exothermic reaction during oxidation. Additionally, this two peaks and mass gradient is steeply change almost simultaneously. This peak and mass change proved phase transformation.

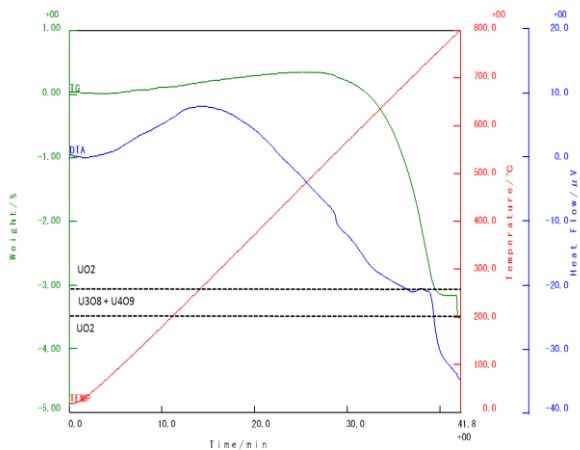


Fig 4. TG-DTA curve of reduction process

In the reduction process, It is only once that the mass gradient changes steeply. Also, DTA line shows one exothermic peak around the black line. Theoretical mass change of  $U_3O_8$  to  $U_4O_9$  is -2.38wt% and mass

change of  $U_3O_8$  to  $UO_2$  is -3.8wt%. In our experiment, there are not flat line around -2.38wt%, In fig 4, Second flat line of TG is around -3.5wt%. Thus, reduction reaction of  $U_3O_8$  is directly change to  $UO_2$ .

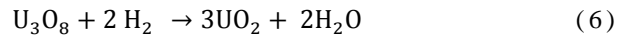
According to other author,  $U_3O_8$  consists of uranium atoms with different oxidation states. one having the value (+4), while the other two (+6). at temperatures above 250°C, undergoes a dismutation reaction, where this compound is oxidized and reduced to  $U_3O_8$  and  $U_4O_9$  at the same time. For  $U_4O_9$  it has 2 uranium ions in oxidation state (+4) and the other 2 in oxidation state (+5). which is unstable under these temperature conditions. Consequently, because of its instability in these conditions, it will be quickly reduced to  $UO_2$  [2]

Enthalpy of formation at standard state

$$\Delta H_{f,UO_2}^\circ = -1085.91 \text{ (kJ/mol)} \quad (1)$$

$$\Delta H_{f,U_4O_9}^\circ = -4512.00 \text{ (kJ/mol)} \quad (2)$$

$$\Delta H_{f,U_3O_8}^\circ = -3574.80 \text{ (kJ/mol)} \quad (3)$$



$$\Delta H_f^\circ (U_3O_8) = -320.07 \text{ (kJ/mol)} \quad (7)$$

$$\Delta H_f^\circ (UO_2) = -54.53 \text{ (kJ/mol)} \quad (8)$$

Using Hess's law both  $UO_2$  oxidation reaction and  $U_3O_8$  reduction reaction are exothermic reaction. From (4) and (5) reaction enthalpy change is (7). Negative means it is exothermic. And from (6) reaction enthalpy change is (8). Thus, both (7) and (8) are exothermic. In  $UO_2$  oxidation process DTA and calculated enthalpy change both show exothermic reaction. However, in  $U_3O_8$  reduction process doesn't match. Calculated enthalpy change(8) is exothermic reaction.[1] Because, Theoretical reverse reaction of the oxidation reaction is a endothermic reaction. This result may show hydrogen has exothermic reaction during measurement. In this study, Due to the reaction of the  $H_2 + O_2 = H_2O$ , calculated enthalpy change is a exothermic.

#### 3.2 Lattice parameter of $UO_2$ and $U_3O_8$ by XRD.

Table 1 shows the results of lattice parameter of  $UO_2$  using Bragg's law and cubic structure equation(9). Average lattice constant value is  $a=5.468(\text{\AA})$ . It is well math with the theoretical lattice parameter  $a=5.4704 \pm 0.0008$ .

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \quad (9)$$

Table. 1. Calculation of  $\text{UO}_2$  lattice values.

Peak	$2\theta$	(hkl)	d	a(Å)
1	28.25	(1,1,1)	3.156	5.467
2	32.73	(2,0,0)	2.734	5.468
3	46.96	(2,2,0)	1.933	5.468
4	55.71	(3,1,1)	1.649	5.468
5	58.42	(2,2,2)	1.578	5.468
6	68.6	(4,0,0)	1.367	5.468
7	75.77	(3,3,1)	1.254	5.468
8	78.1	(4,2,0)	1.223	5.468
9	87.28	(4,2,2)	1.116	5.468
10	94.11	(5,1,1)	1.052	5.468
11	105.67	(4,4,0)	0.967	5.468
12	112.9	(5,3,1)	0.924	5.468
13	115.4	(6,0,0)	0.911	5.468
14	125.99	(6,2,0)	0.865	5.468
15	134.97	(5,3,3)	0.834	5.468
16	138.28	(6,2,2)	0.824	5.468

Table 2 shows the results of lattice parameter of  $\text{U}_3\text{O}_8$  using Bragg's law and orthorhombic structure equation(10). Average lattice constant values are  $a=6.717(\text{Å})$ ,  $b=4.147(\text{Å})$ ,  $c=11.959(\text{Å})$ . It is well matched with the theoretical lattice parameters  $a=6.751(\text{Å})$ ,  $b=4.14607(\text{Å})$ ,  $c=11.978(\text{Å})$ .

$$\frac{1}{d^2} = \frac{d^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (10)$$

Table. 2. Calculation of  $\text{U}_3\text{O}_8$  lattice values.

Lattice parameter	$2\theta$	(hkl)	d	Lattice values(Å)
c	21.41	(0,0,1)	4.147	4.147
a	26.52	(2,0,0)	3.358	6.717
c	43.63	(0,0,2)	2.073	4.146
b	45.47	(0,6,0)	1.993	11.959
a	54.62	(4,0,0)	1.679	6.716

We can calculate the density of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  using the measured lattice parameter, volume of unit cell of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  is  $163.4879 \times 10^{-24} \text{ cm}^3$  and  $334.8809 \times 10^{-24} \text{ cm}^3$ . The mass of unit cell is determined by the number of uranium and oxygen in the unit cell. unit cell of  $\text{UO}_2$  contains four uranium and eight oxygen, and unit cell of  $\text{U}_3\text{O}_8$  contains eight uranium and sixteen oxygen. Thus, The mass of unit cell of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  is  $1793.14 \times 10^{-24} \text{ g}$  and  $2795.691 \times 10^{-24} \text{ g}$ . The density were determined by using volume and mass of unit cell. As a result of calculation using volume and mass of unit cell, the density of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  is  $10.9680 \text{ g/cm}^3$  and  $8.3501 \text{ g/cm}^3$ . During oxidation of  $\text{UO}_2$ , the density decreased by about 30%, which means a volume increase of about 30%.

### 3.3 Result of solid solution $\text{Zr}_y\text{U}_{1-y}\text{O}_2$ by SEM and EDX

The morphologic images obtained from SEM (Figure 6.) showed the particles of solid solutions were plate-type and the particle sizes were approximately  $2 \mu\text{m}$ . No significant difference in the morphologies of both samples were observed.

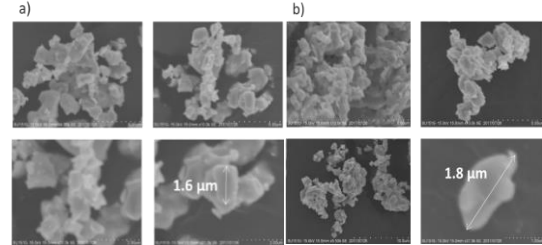


Fig 6. Result of SEM analysis

According to SEM/EDX images of synthesized  $\text{Zr}_y\text{U}_{1-y}\text{O}_2$  solid solution ( $y = 0.05$ , Figure 2), uranium and zirconium seem to be distributed homogeneously.

However, EDX results were  $\text{Zr}_{0.0311}\text{U}_{0.09689}\text{O}_2$  and  $\text{Zr}_{0.0537}\text{U}_{0.09462}\text{O}_2$  for  $y = 0.05$  and  $0.1$ , respectively. Determined values (0.0311 and 0.0537) by EDX were less than initial values (0.05 and 0.1).

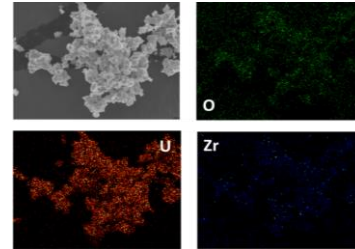


Fig 7. Result of EDX analysis

We are able to notice that it is short time to be  $\text{U}_{1-y}\text{Zr}_y\text{O}$ . Because, Self diffusion of U and O in  $\text{UO}_2$  and diffusion of Zr into  $\text{UO}_2$  may play an important role in the formation of solid solution. According to other author, the diffusivity of anions which constitute the simple cubic structure is much higher than that of cations on the face-centered cubic structure[3], In the comparison of self diffusion of U in  $\text{UO}_2$  and diffusion of Zr into the  $\text{UO}_2$ . The diffusion of Zr is faster than self diffusion of U in  $\text{UO}_2$ [4]. Thus, the rate limiting step in the formation of solid solution may be the self diffusion of U in  $\text{UO}_2$ . So we need more annealing time considering self diffusion coefficient of U in  $\text{UO}_2$  for formation of solid solution.

### 3.4 Lattice parameter of solid solution $\text{Zr}_y\text{U}_{1-y}\text{O}_2$ by XRD.

XRD provided the structural information of  $\text{Zr}_y\text{U}_{1-y}\text{O}_2$  solid solutions. In Fig 8, Very similar peak positions in solid solutions were obtained as compared to  $\text{UO}_2$ . This represents the main structures of the  $\text{Zr}_y\text{U}_{1-y}\text{O}_2$ .

$y\text{O}_2$  solid solutions are identical in the absence and the presence of Zr ( $y = 0.05$  and  $0.1$ ). According to the  $\text{UO}_2\text{-ZrO}_2$  pseudo binary phase diagram[5], no change in the structure and the cubic structure was expected.

$$\frac{1}{d^2} = \frac{\frac{1}{h^2} + \frac{1}{k^2} + \frac{1}{l^2}}{a^2} \quad (11)$$

However, Even if it has a same structure, the spacing between two layer of lattice can be change. In Fig 8. The peak move to right side as Zr portion increase. We can calculate the lattice parameter by using equation (11) and each XRD peak.

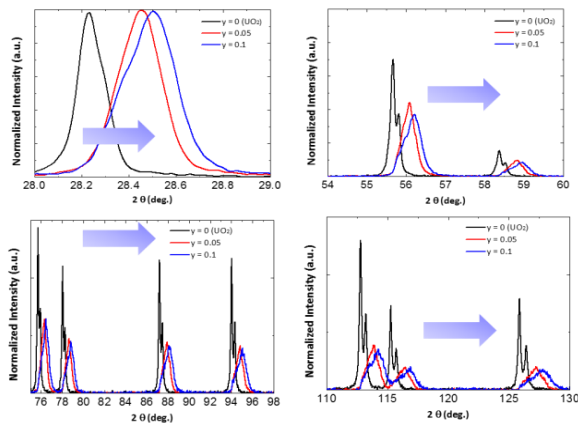


Fig 8. Result of XRD analysis

Fig 9 is a result of lattice parameter. Lattice parameter of  $\text{Zr}_y\text{U}_{1-y}\text{O}_2$  were 5.43458 and 5.42422 Å for  $y = 0.05$  and  $0.1$ . The lattice parameter had a decrease tendency as increasing Zr portion. Thus, volume of solid solution is decrease compared with  $\text{UO}_2$ . Shrinking of unit cell may be due to the intrusion of Zr

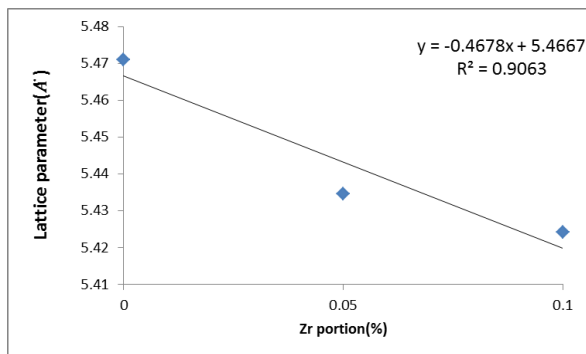


Fig 9. Lattice parameter of solid solution

Zr has a smaller radius than U. Theoretical radius of Zr and U is 0.988 Å and 1.148 Å. So volume of solid solution is decreased as increase the Zr ratio. According to Vegard's law, unit cell parameters should vary linearly with composition for a continuous substitute solid solution in which atoms or ions that substitute for each other are randomly distributed[4 5]. In Fig 10, coefficient of determination is 0.9814. Thus, The

measured lattice parameter is good agreement with Vegard's Law.

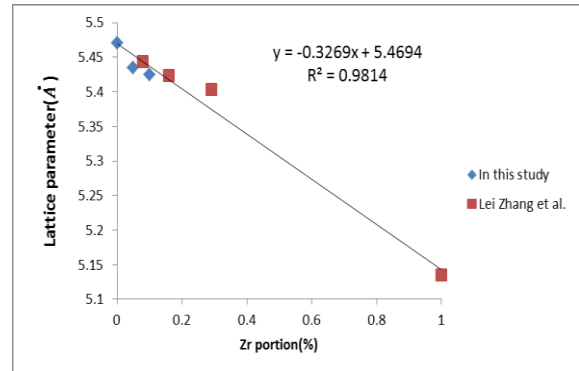


Fig 10. Linear regression of lattice parameter

#### 4. Conclusion

In the first experiment, we are able to get the sense of phase change of uranium oxide as measuring weight from TG-DTA experiment. When  $\text{UO}_2$  is in oxidation to  $\text{U}_3\text{O}_8$ , it has a change of structure. By using XRD, we can get the structure of  $\text{UO}_2, \text{U}_3\text{O}_8$  and the lattice parameter of that. By using the lattice parameter, we can notice that there is a volume expansion during the oxidation process of  $\text{UO}_2$  to  $\text{U}_3\text{O}_8$ . When we calculated the enthalpy of oxidation and reduction process, both reaction are exothermic reaction.

In the second experiment, By using EDX, we measured a ratio of Zr and U in the solid solution. the measured ratio is less than initial value(0.05 and 0.1). The diffusion coefficient of U is much smaller than O in  $\text{UO}_2$ . So U is the rate limiting step in formation of solid solution. we need more annealing time for formation of solid solution. By using XRD, we are able to guess the effect of cation to the lattice parameter. The lattice parameter had a decrease tendency as increasing Zr. Thus Shrinking of unit cell may be due to the intrusion of Zr.

#### 5. Reference

- [1] Bruce S. (1982). Hemingway, Thermodynamic properties of selected uranium compounds and aqueous species at 298.15 K and 1 bar and at higher temperatures Preliminary models for the origin of coffinite deposits. U.S. Geological Survey.
- [2] Reduction Kinetics of Uranium Trioxide to Uranium Dioxide Using Hydrogen Pedro Orrego Alfaro<sup>1</sup>, José Hernández Torres<sup>1</sup>, Fernando Puchi Thiele<sup>2</sup>, World Journal of Nuclear Science and Technology, 2015, 5, 149-156
- [3] Ken Ando and Yasumichi Oishi. "Diffusion characteristics of actinide oxides." Journal of nuclear science and technology (1983)
- [4] R. Perriot, X.-Y. Liu, C. R. Stanek, and D. A. Andersson, "Diffusion of Zr, Ru, Ce, Y, La, Sr and Ba fission products in  $\text{UO}_2$ ." Journal of Nuclear Materials (2015).
- [5] Lei Zhang, Anna Shelyug, and Alexandra Navrotsky. "Thermochemistry of  $\text{UO}_2\text{-ThO}_2$  and  $\text{UO}_2\text{-ZrO}_2$  fluorite solid solutions." The Journal of Chemical Thermodynamics (2017).