Experiments of Oxidation and Reduction of Uranium Oxide and Solid Solution of UO_2-ZrO_2 in Tohoku University

Tae hoon Kim[a], Kwangheon Park[a*], Ju Hyeong Lee[a], Hyoung gyu Park[a], Jisu Kim[a] , Hyuk jin Song[b], Chan ki Lee[c], Do kyu Kang[c], Hyeon jun Jeong[c]
[a] *Department of Nuclear Engineering, Kyunghee University, Kyunggi-do, 446-701, Korea*
[b] *Dongguk Universiyu, 707, Seokjang-Dong, Gyeongju, Korea*
[c] *Ulsan National Institute of Science and Technology, 50 UNIST-gil, Ulju-gun, Ulsan, Korea*
[*] *Corresponding author: khpark@khu.ac.kr*

1. Introduction

Zirconium (Zr) is one of important elements in the composition used in the nuclear fuels. The properties of uranium oxide that contains Zr has been studied for a long time, since it appears in the gap between the pellet and the cladding in normal conditions and accident conditions as well. Recently, the Fukushima accident gave another motivation for the study of its properties related to the thermodynamic and kinetic analyses. We did a basic study on the solid solution formation from the mixture of UO_2 + ZrO_2.

In first experiment, the oxidation behavior of UO_2 in air was analyzed using TG-DTA by raising the temperature from room temperature to 500℃ (Heating rate: 10K/min). After oxidation to U_3O_8, we reduced U_3O_8 to UO_2 again with Ar + 10% H_2 gas. In this experiment, we were able to check the transition of weight and thermal capacity at material.

After doing that experiment, we used XRD to analyze the structure of material. In our case, the lattice parameter of UO_2 is 5.4695Å and the experimental density is 10.9525g/cm3. The theoretical density is 10.96 g/cm3. And the structure of UO_2 is fluorite cubic. Comparing to that, the experimental density of U_3O_8 is 8.3962g/cm3 and the theoretical density is 8.3g/cm3. U_3O_8 has orthorhombic structure. The lattice parameters are 6.72 Å, 11.96 Å and 4.15 Å [1].

In second experiment, we studied the solid solution formation from the mixture of UO_2 + ZrO_2. The formation reaction was done at 1400℃, under Ar + 10% H_2 gas (20.0ml/min) for 6 hours. We used SEM to check the formation of the solid solution and to measure the size of particles. XRD analysis was done to see the lattice parameter change with respect to the Zr content.

2. Methods and Results

2.1 Procedure of UO_2 Oxidation and Reduction

First, we prepared fine UO_2 powder to be oxidation easily (Fig.1). Before making the fine UO_2, we should check the weight of boat to get exact amount of UO_2. After making the fine UO_2 powder, put the powder on the boat to measure the weight of UO_2. (Fig.2)

Fig.1

Fig.2

Second, put the sample on holder in TG-DTA. (Fig.3) Set the TG-DTA below condition for Oxidation experiment. The gas (Ar + 2% O_2) flow rate was 20ml/min and the heating rate is 10K/min. After doing oxidation, Set the TG-DTA below condition for Reduction experiment. The gas (Ar + 10% H_2) flow rate is 20ml/min and the heating rate is 10K/min like oxidation. (Fig.4)

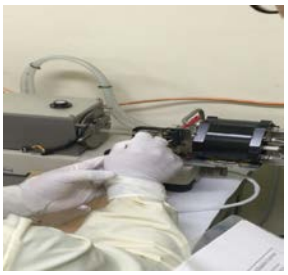

Fig.3

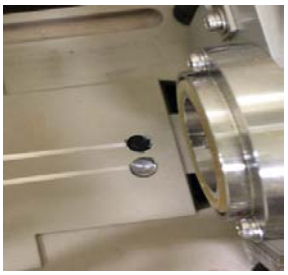

Fig.4

After the oxidation process, withdraw the sample from TG-DTA and check the weight. For reduction of the sample, we change from Ar + 2% O_2 to Ar + 10% H_2.

2.2 Procedure of UO_2 + ZrO_2 solid solution

First, we have to put 0.2g of UO_2 and 0.005g of ZrO_2 on the boats to make the 95% UO_2 + 5% ZrO_2 and 0.2g of UO_2 and 0.01g of ZrO_2 on the boats to make the 90% UO_2 + 10% ZrO_2. (Fig.5) After putting those materials, we have to grind for 20minutes to mix those materials. (Fig.6)

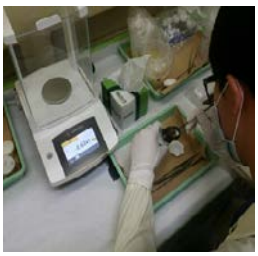

Fig.5

Fig.6

For making UO_2 + ZrO_2 solid solution sample, prepare two samples of UO_2 and ZrO_2, and then, measuring weight, grinding respectively. $U_{1-y}Zr_yO$ powder was installed in the furnace (Fig.7). To make reaction in heat treatment apparatus, the apparatus is supposed to be evacuated first. And then, we put the Ar + 10% H_2 to have reduction process. The process of transition of temperature is RT to 1000℃ within 2h, 1300℃ within 1h, 1400℃ with 0.5h and 1400℃ for 1h (Fig.8)

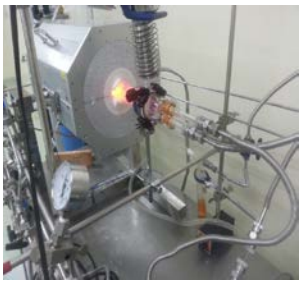

Fig.7

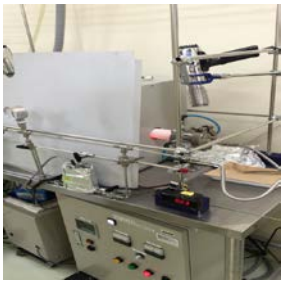

Fig.8

2.3 Analysis

The objective of the first experiment is to see the change of UO_2 by using TG-DTA and XRD (Fig.9). By using TG-DTA, we can see the change of weight and thermal capacity at material with heating UO_2 up. And By using XRD, we can study detailed structure and composition of UO_2 in various situations.

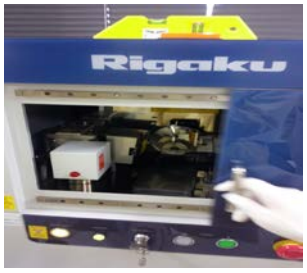

Fig.9

The objective of the second experiment is to see the influence of cation to the lattice parameter of compound (UO_2 + ZrO_2). We use XRD, SEM to analyze that material. By using XRD, we can study the structure of compound same as first experiment. By using SEM, we can measure the size of the particles and the ratio of that compound how they are well mixed.

When we use SEM, we have to sample to be coated with Au, Pd to make conductor. (Fig.10, 11)

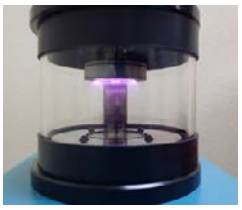

Fig.10

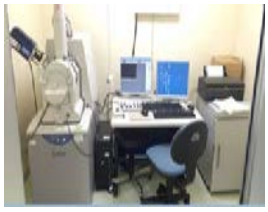

Fig.11

3. Result and discussion

3.1 Results of UO_2 Oxidation

At the first experiment, when we make UO_2 powder, we can see the color of powder. It has brown color. The first amount of UO_2 which is before doing experiment is 18.9mg. In our case, the kinetic domain is first one that UO_2 change to UO_{2+x}. Because it takes short time to be second domain or others. So it has 2 mechanisms which are to be U_4O_9 and U_3O_8. We can see that the weight change of UO_2 to U_4O_9 is around 1.48wt%. And the weight change of UO_2 to U_3O_8 is around 3.95wt%. (Fig.12)

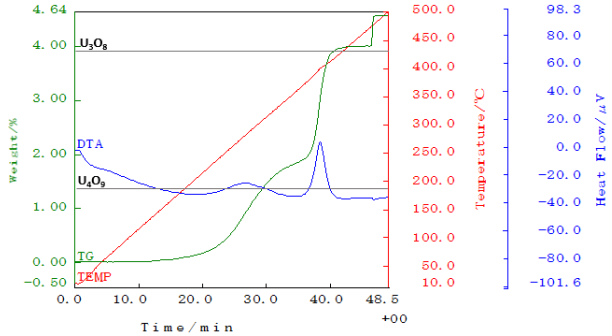

Fig.12 TG-DTA curve of UO_2 oxidation in Ar-O_2 depending on temperature, Heat rate 10K/min

Also, we can see the change of thermal capacity. It has a exothermic peak around 400℃. UO_2 is fluorite structure and the diffusion into the lattice occurs rapidly upon exposure to an oxygen environment. UO_{2+x} is not stable formation, thus it can go to another stable forms depending on oxygen partial pressure and temperature. And the oxidation occurs within the outer of UO_2 sample. It makes a barrier to block diffusion of oxygen into inner sample of UO_2. But, as temperature goes up, the diffusion overcomes the barrier and whole sample can be converted to U_3O_8 finally. And we can see the obvious exothermic peak of DTA curve in our data. (Fig. 12)

3.2 Results of U_3O_8 Reduction

In the reduction situation, we are able to see just one mechanism which is to be UO_2 from U_3O_8.(Fig.13) The initial amount of UO_2 is 19.5mg. When we see the Fig.13, we can see the weight change of U_3O_8 to UO_2 is around -3.8wt%.

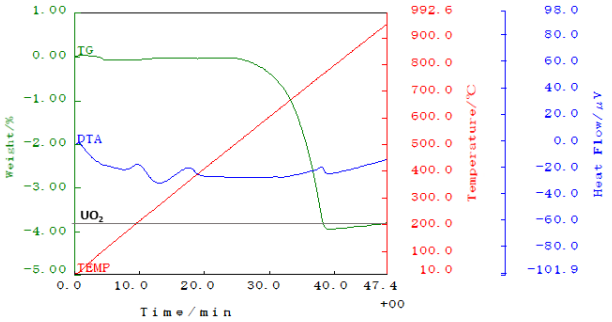

Fig.13 TG-DTA curve of U_3O_8 reduction in Ar-H_2 depending on temperature, Heat rate 10K/min

We can see the transition of thermal capacity of U_3O_8. It has no tendency when it is to be UO_2 from U_3O_8. However, depending on the temperature, weight loss occur at around 500℃. From the weight loss curve, we can confirm U_3O_8 changes to UO_2. However, there is no clear endothermic peak of DTA. We can only estimate reduction occurrence using TG curve and compare it with our computation about weight loss, when fully reduction occur. The computation values are derived from calculating the number of moles of uranium. According to the ratio of uranium oxide, for example U_3O_8 has O/U=8/3, simply calculate that how much of oxygen is needed or released.

3.3 Results of XRD analysis of UO_2

When we use XRD to know the lattice parameter, we can get the information of 2theta and (h, k, l). (Table.1)

Table 1 : UO2 of miller indices in the experiment

Peak No.	2θ	d	h k l	$h^2+k^2+l^2$	a(Å)
1	28.23	3.158	1 1 1	3	5.4698
2	32.72	2.735	2 0 0	4	5.4700
3	46.94	1.934	2 2 0	8	5.4702
4	55.69	1.649	3 1 1	11	5.4691
5	58.4	1.579	2 2 2	12	5.4698
6	68.57	1.367	4 0 0	16	5.4680

By using the Bragg's law and we know the structure of that one, we can calculate the lattice parameter of UO2. The lattice parameter of UO_2 is 5.4695Å. Comparing to UO_2, U_3O_8 has different structure, which is orthorhombic. It has 3 different lattice parameters because it is orthorhombic. It has 6.72Å, 11.96Å and 4.15Å [1]. Anyway, we know the lattice parameters of UO_2 and U_3O_8. So we can calculate the volume of lattices and each density.

3.3 Results of XRD,SEM analysis of UO_2 +ZrO_2

At the second experiment, we use UO_2 + ZrO_2 materials. The color of ZrO_2 is white. First, we put and measure the weight of UO_2 and ZrO_2 separately. To make 95% UO_2 + 5% ZrO_2, we put 0.1940g of UO_2 and 0.0043g of ZrO_2 in the boats. And to make 90% UO_2 + 10% ZrO_2, we put 0.1960g of UO_2 and 0.0104g of ZrO_2. After heating them up to make compound, the net weight of 95% UO_2 + 5% ZrO_2 is changed to 0.1751g and the net weight of 10% UO_2 + 10% ZrO_2 is changed to 0.1883g. So we can guess that the mass which is before experimented is bigger than the mass which is after being compound ($U_{1-y}Zr_yO$). Also the color of that material has been changed to dark brown from brown.

When we see Fig.14, we can measure the size of particles, which are UO_2, ZrO_2 and $U_{1-y}Zr_yO$. And also we are able to notice that it is short time to be $U_{1-y}Zr_yO$ without UO_2, ZrO_2. Because when we see Fig.14, there are pure UO_2, ZrO_2 and $U_{1-y}Zr_yO$.

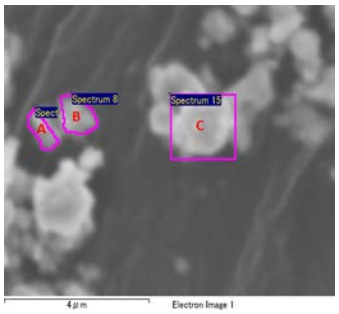

Fig.14 Micro view of UO_2, ZrO_2 and $U_{1-y}Zr_yO$ in SEM

The sizes of UO_2, ZrO_2 and $U_{1-y}Zr_yO$ are around 0.73μm, 1.02 μm and 1.89 μm.

By using XRD, we are able to measure the lattice parameter depending on the ratio of compound. To get the lattice parameter, we also use Bragg's law like first experiment.

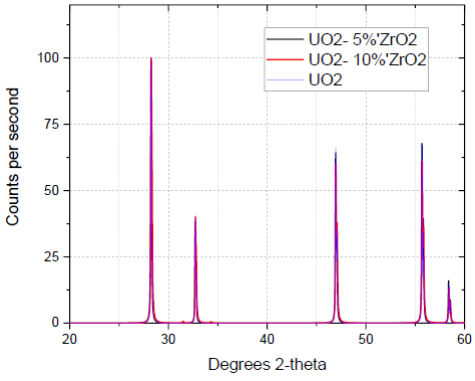

Fig.15 XRD pattern of UO_2+ZrO_2 compounds

When we see Fig.15, there are no big differences between compounds and UO_2. Conclusively, 2theta of 95% UO_2 + 5% ZrO_2 and UO_2 is almost same. However 2theta in 90% UO_2 + 10% ZrO_2 has bigger comparing

to others. So 90% UO_2 + 10% ZrO_2 has smaller lattice parameter than others.

By calculating the lattice parameter, 95% UO_2 + 5% ZrO_2 has a lattice parameter of 5.4728Å and 90% UO_2 + 10% ZrO_2 has a lattice parameter of 5.4699 Å. The crystal radius of U and Zr are 0.87Å, 0.86Å. So we can know that the smaller the size of cation, the smaller the size of lattice parameter.

According to other author, this reaction is related about diffusion coefficient. In literature, the diffusion coefficient of O in UO_2 at 1400℃ is 10^{-7} cm^2/s and the diffusion coefficient of U in UO_2 at 1400℃ is 10^{-13} cm^2/s [2]. It is well known that values of cation diffusion coefficients are much lower than those associated with anion diffusion coefficient. For in this process it is the cation transport that is the rate-limiting step.

5. 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. The data which is related about TG is correct with what we know. When UO_2 is in oxidation to U_3O_8, its weight is getting bigger. By using XRD, we can get the structure of UO_2 an U_3O_8 and the lattice parameter of them. When we calculated the density of UO_2 and U_3O_8, we can know that the density of UO_2 is higher than the density of U_3O_8. The structure of UO_2 is fluorite cubic and the structure of U_3O_8 is orthorhombic. When we check the weight of UO_2 and U_3O_8, we took them in the air condition. So, some of them were evaporated a little bit. It also impacted to the result of that experiment.

In the second experiment, we used XRD, SEM to get information of $U_{1-y}Zr_yO$. When we heated $U_{1-y}Zr_yO$ up at 1400℃in 1h, we can know it is not adequate to get high ratio of $U_{1-y}Zr_yO$. Because when we see Fig 14, there are UO_2 and ZrO_2 with $U_{1-y}Zr_yO$. By using XRD, we are able to guess the effect of cation to the lattice parameter. The smaller the size of cations is, the smaller the lattice parameter is. So, 95% UO_2 + 5% ZrO_2 has larger lattice parameter than 90% UO_2 + 10% ZrO_2 in our experiment. And we know the diffusion coefficient of U and O in UO_2. The diffusion coefficient of U is much smaller than O in UO_2. So U is the rate limiting step in UO_2 compound. Namely, U governs the interaction in UO_2. There are human errors, other environment error and etc. Those would be affecting to the results.

REFERENCES

[1] Rousseau, G., Desgranges, L., Charlot, F., Millot, N., Niepce, J. C., Pijolat, M. & Bérar, J. F. (2006). A detailed study of UO_2 to U_3O_8 oxidation phases and the associated rate-limiting steps. Journal of nuclear materials, *355*(1), 10-20.

[2] Sakka, Y., Oishi, Y., Ando, K., & Morita, S. (1991). Cation interdiffusion and phase stability in polycrystalline tetragonal ceria–zirconia–hafnia solid solution. Journal of the American Ceramic Society, 74(10), 2610-2614.