UO$_2$-ZrO$_2$ interaction in oxidation and reduction conditions

Geon yong Lee[a], Kwang heon Park[a*], Ju hyeong Lee[a], Hyoung gyu Park[a]
*[a]Department of Nuclear Engineering, Kyung Hee University, 1732 Deokyoungdaero, Giheung-gu, 17104, Yongin-Si,
Republic of Korea*
[*]Corresponding author: kpark@khu.ac.kr

1. Introduction

Understanding the interaction between UO$_2$ and ZrO$_2$ is very important. At high fuel burnup. there is a possibility that the UO$_2$ pellet will expand and contact the cladding. At that time, there is a thin ZrO$_2$ layer on the inner side of the cladding.

In addition, in the case of defective nuclear fuel, the inside of the cladding is oxidized by steam, and the oxide film may grow and react with the UO$_2$ pellet. In the situation mentioned above, ZrO$_2$ and UO$_2$ form a bonding layer between the cladding and the pellet [1]

Due to the long-term storage of the high burnup spent nuclear fuel, an analysis of the formation and behavior of theses bonding layer is important

In our study, we conducted experiment which is related to the interaction between UO$_2$ and ZrO$_2$. The temperature was heated from R.T to 1350℃ and 1400℃ using gas with various oxygen pressures. After heat treatment, we used X-ray diffraction(XRD) to analyze the structure of the material.

2. Materials amd Method

2.1 Sample preparation

First. We oxidized natural UO$_{2+x}$ and then reduced the sample under argon atmospheric conditions with 4% hydrogen, this was done to obtain UO$_{2.0}$ by using a furnace.

Second. UO$_{2.0}$ and ZrO$_2$ powders were blended for 20 minutes with the same molar ratio. After blending, the sample was put into the furnace for heat treatment.

Heat treatment followed. first, sample was heated up to 1350 ℃ and 1400℃ at 10℃/min and then maintained for three hour. After heat treatment, it was cooled down to room temperature. During the heat treatment we added the gas at 100ml/min for the oxidizing and reducing condition.

In the first experiment, For a comparison of the X-ray diffraction pattern in the oxidation and reduction condition. We conducted the experiment using Ar+4%H$_2$ and air in 1400℃

Table 1. Condition of the experiment 1

Gas	Temperature	Flow Rate	Heating time
Ar + 4% H$_2$	1400℃	100 ml/min	1 hour
Air	1400℃	100 ml/min	1 hour

In the second experiment, For a comparison of the X-ray diffraction pattern in the different partial pressures of oxygen. We conducted the experiment using the air,Ar+H$_2$O and 99%Ar in 1350℃

Table 2. Condition of the experiment 2

Gas	Temperature	Flow Rate	Heating time	Partial pressure of oxygen(mmHg)
Air	1350 ℃	100 ml/min	3 hours	159
99% Ar	1350 ℃	100 ml/min	3 hours	7.6
Ar+H$_2$O	1350 ℃	100 ml/min	3 hours	22.8

When we used the Ar+H$_2$O, we used a bubbler to get the Ar to contain moisture. The equipment is shown in the Figure 1.

There are two inlet in front of the valve. One is a normal inlet, and the other line is passes through water. The bubbler get Ar to contain moisture.
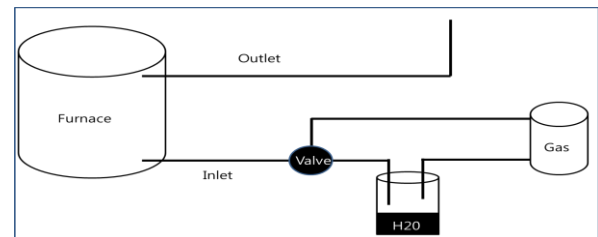

Fig. 1. The experimental equipment, which has a bubbler and normal inlet.

2.2 Measurment

After heat treatment, we made an XRD sample. By using XRD, we could analyze the structure of the sample. Measurement was conducted in the range of 20° to 140° of 2-theta. We implemented 0.01° increments of 2-theta per second.

To analyze the formation of the solid solution, UO$_2$ and ZrO$_2$ (the starting material) were also measured by using XRD. Measurement was carried out by following the same procedure as mentioned above

3. Results and Discussion

3.1 XRD result of the experiment 1

After measurement, we could obtain the XRD pattern of the sample. Then, we analyzed the pattern by using

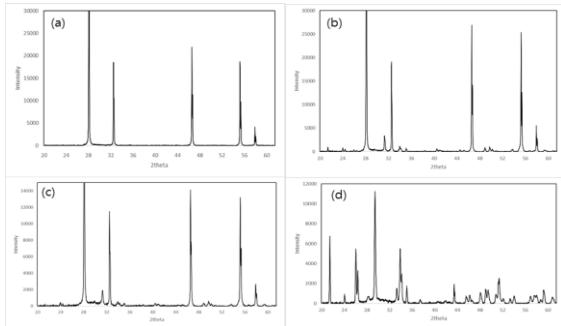EVA. Figure 2-(a) shows an XRD pattern of $UO_{2.0}$ we can see five sharp peaks.

Fig 2. (a)$UO_{2.0}$ X-ray diffraction pattern.(b) Starting material(UO_2+ZrO_2 mixture).(c) UO_2+ZrO_2 1400℃ for 1h in Ar+4% H_2. (d)UO_2+ZrO_2 1400℃ for 1h in Air

In figure 2-(b). we can see five UO_2 peaks and monoclinic ZrO_2 peak. This sample was the starting material and this pattern was compared with other results.

After the reduction condition experiment. XRD results is Fig 2-(c). In the XRD pattern. there was no difference between it and the starting material.
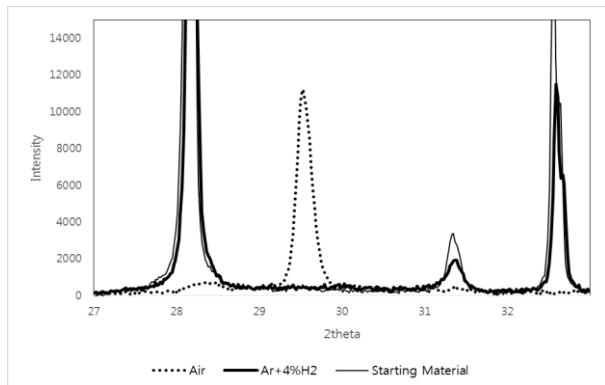

Fig3. A comparison of the pattern in the oxidation and reduction conditions.

Figure 2-(d) shows the XRD data for UO_2+ZrO_2 at 1400℃ one hour in Air. Compared with the experimental result of the reduction condition. In Figure 3, we can see that UO_2 peak moved to a high angle. This shift of the peak's position was due to the formation of a solid solution. Under the same conditions, it was confirmed that the solid solution formed easily in the oxidation condition.

3.2 XRD result of the experiment 2

Fig 4-(a) shows the result of the XRD for UO_2+ZrO_2 at 1350℃ for three hour in air. There are three phases(cubic-UO_2,monoclinic-ZrO_2,orthorhombic-U_3O_8). UO_2 is oxidized to U_3O_8. therefore we can see the U_3O_8 peak in the Figure 4-(a). U_3O_8 has an orthorhombic structure.

U_3O_8 does not react with ZrO_2 to form a solid solution because it has a different structure. However it decomposed at a high temperature more than 1300℃ and it present in UO_{2+x} form. The decomposed UO_{2+x} react with ZrO_2 to form a cubic solid solution
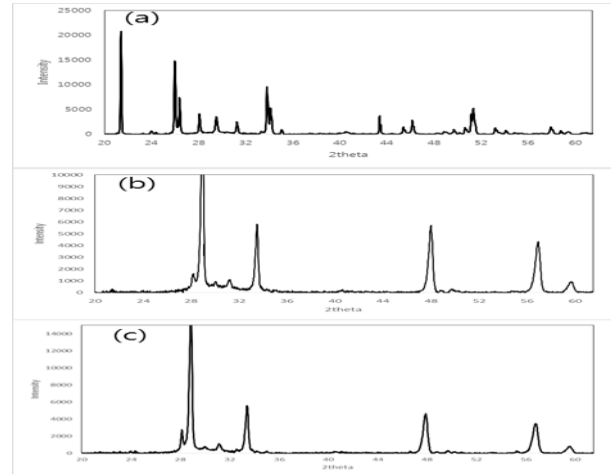

Fig4. (a)UO_2+ZrO_2 1350℃ for 3h in Air.(b) 2+ZrO_2 1350℃ for 3h in Ar+H_2O.(c) UO_2+ZrO_2 1350℃ for 3h in Ar

Figure 4-(b) and Figure 4-(c) show the XRD data for UO_2+ZrO_2 at 1350℃ for three hour in Ar+H_2O and UO_2+ZrO_2 at 1350℃ for three hour in Ar. These two XRD patterns had very similar patterns.UO_2 did not oxidize like an air condition sample in Figure 4-(a). However it was confirmed that UO_2 peak intensity, which was near 28 degrees was reduced. At the same time, the solid solution peak can be seen moving at a high angle. This shift means that the lattice parameter is decreased.

Figure 5 shows the four XRD patterns. We can see that the intensity of the UO_2 peak, at around 28 degrees, decreases and that peak moves to high angle.

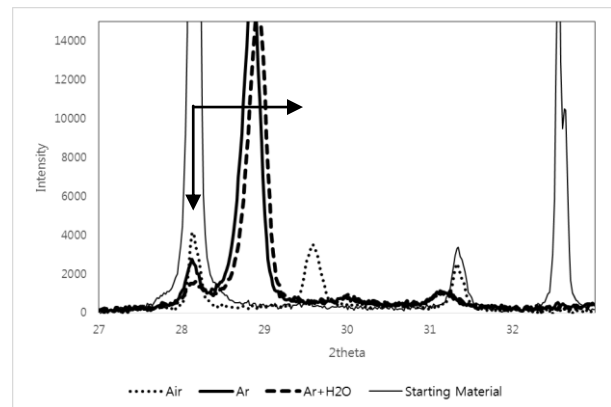This phenomenon is related to the partial pressure of oxygen.

Fig5. A comparison of the pattern of the starting material and a solid solution in the oxidation condition.

As the partial pressure of oxygen increases, $UO_{2.0}$ becomes UO_{2+x}. As the oxygen interstitial concentration increases, The uranium vacancy concentration increases. As a result, a defect of uranium increases due to a Schottky defect and a Frankel defect.[2]. Thus, increasing the uranium vacancy with an increasing partial pressure of oxygen caused Zr to react with UO_2 better.

Zr has a smaller radius than U. Theoretical radii of Zr and U are 0.988 Å and 1.148 Å. respectively. So, the volume of the solid solution decreased as the Zr ratio increased[3]. Therefore, as the partial pressure of oxygen increased, the peak shifted to a high angle. This resulted in the unit cell shirinking.

4. Conclusions

As a result of the two experiments, we found that UO_2 and ZrO_2 react more easily in the oxidizing condition than in the reduction condition. The reaction of UO_2 and ZrO_2 in the reduction condition requires longer reaction times or higher temperatures than the oxidation condition.

We conducted experiments using Ar, $Ar+H_2O$ and air according to the oxygen pressure. As the partial pressure of oxygen increased, Zr reacted more easily to uranium. Therefore, the peak shifted to a high angle and the lattice parameter was decreased

REFERENCES

[1] K.T Kim, UO2/Zry-4 chemical interaction layers for intact and leak PWR fuel rods. Journal of Nuclear Materials 404 (2010) 128–137

[2] L. Desgranges , M. Gramond, C. Petot, G. Petot-Ervas, P. Ruello, B. Saad, Characterisation of uranium vacancies in hyper stoichiometricuranium dioxide, Journal of the European Ceramic Society 25 (2005) 2683–2686

[3] 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 UO2." Journal of Nuclear Materials (2015).