**UO₂-ZrO₂ interaction in oxidation and reduction conditions**

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1. Introduction

Understanding the interaction between UO₂ and ZrO₂ is very important. At high fuel burnup, there is a possibility that the UO₂ pellet will expand and contact the cladding. At that time, there is a thin ZrO₂ 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 UO₂ pellet. In the situation mentioned above, ZrO₂ and UO₂ 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 these bonding layer is important.

In our study, we conducted experiment which is related to the interaction between UO₂ and ZrO₂. The temperature was heated from R.T to 1350°C and 1400°C using gas with various oxygen pressures. After heat treatment, we used X-ray diffraction (XRD) to analyze the structure of the material.

2. Materials and Method

2.1 Sample preparation

First. We oxidized natural UO₂₂+x and then reduced the sample under argon atmospheric conditions with 4% hydrogen, this was done to obtain UO₂₀ by using a furnace.

Second. UO₂₀ and ZrO₂ 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 °C and 1400°C at 10°C/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%H₂ and air in 1400°C

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temperature</th>
<th>Flow Rate</th>
<th>Heating time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar+4%H₂</td>
<td>1400°C</td>
<td>100 ml/min</td>
<td>1 hour</td>
</tr>
<tr>
<td>Air</td>
<td>1400°C</td>
<td>100 ml/min</td>
<td>1 hour</td>
</tr>
</tbody>
</table>

Table 1. Condition of the experiment 1

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+H₂O and 99%Ar in 1350°C

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temperature</th>
<th>Flow Rate</th>
<th>Heating time</th>
<th>Partial pressure of oxygen(mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>1350 °C</td>
<td>100 ml/min</td>
<td>3 hours</td>
<td>159</td>
</tr>
<tr>
<td>99% Ar</td>
<td>1350 °C</td>
<td>100 ml/min</td>
<td>3 hours</td>
<td>7.6</td>
</tr>
<tr>
<td>Ar+H₂O</td>
<td>1350 °C</td>
<td>100 ml/min</td>
<td>3 hours</td>
<td>22.8</td>
</tr>
</tbody>
</table>

Table 2. Condition of the experiment 2

When we used the Ar+H₂O, 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.](image)

2.2 Measurement

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, UO₂ and ZrO₂ (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.

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.

3.2 XRD result of the experiment 2

Fig 4-(a) shows the result of the XRD for UO$_2$+ZrO$_2$ at 1350°C for three hour in air. There are three phases(cubic-UO$_2$,monoclinic-ZrO$_2$,orthorhombic-U$_2$O$_8$). UO$_2$ is oxidized to U$_2$O$_8$. therefore we can see the U$_2$O$_8$ peak in the Figure 4-(a). U$_3$O$_8$ has an orthorhombic structure.

U$_3$O$_8$ 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°C and it present in UO$_{2+x}$ form. The decomposed UO$_{2+x}$ react with ZrO$_2$ to form a cubic solid solution

Figure 4-(b) and Figure 4-(c) show the XRD data for UO$_2$+ZrO$_2$ at 1350°C for three hour in Ar+H$_2$O and UO$_2$+ZrO$_2$ at 1350°C 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.
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 shrinking.

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$_2$O 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