

Hyper-stoichiometric UO_2 interaction with Zry4 at high temperatures

Geon Yong Lee, Kwang Heon Park*

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

The interaction between UO_2 and Zirconium cladding is very important in normal and off-normal states. At high fuel burnup, there is a possibility that UO_2 pellets will expand and contact the cladding. When Zr cladding contacts UO_2 pellets in this way, it absorbs the oxygen from the UO_2 and becomes oxidized. Meanwhile, the UO_2 is reduced to UO_{2-x} and partially produces a eutectic phase. Above $800^\circ C$, β -Zr is in a stable phase but if it is then oxidized to α -Zr, the cladding becomes brittle.

UO_2 interaction with Zr cladding above $1200^\circ C$ has been reported to form five layers, namely $[UO_2]$, $[\alpha-Zr+(U-Zr)]$, $[(U-Zr)]$, $[\alpha-Zr]$, and $[\beta-Zr]$ [1]. However, hyper-stoichiometric UO_2 (UO_{2+x}) forms a different layer than stoichiometric UO_2 ($UO_{2.0}$) because UO_{2+x} is more oxidized than $UO_{2.0}$ and is not reduced to UO_{2-x} through contact with the Zr cladding.

So, hyper-stoichiometric UO_2 (UO_{2+x}) and Zry4 forms four layers. Namely $[UO_2]$, $[(U-Zr)O_2]$, $[\alpha-Zr]$, and $[\beta-Zr]$

In our study, we conducted an experiment concerning the interaction between UO_2 and Zry4. The temperature was increased from room temperature to $1300^\circ C$ using $Ar+4\%H_2$ gas. After the heat treatment, we used X-ray diffraction (XRD) to analyze the structure of the material and an optical microscope (OM) to analyze the thickness of the interaction layer.

2. Materials and Methods

To begin, a UO_{2+x} disk was stacked on top of Zry4. A vacuum was created in the furnace using a vacuum motor, and $Ar+4\%H_2$ gas was then introduced into the furnace to prevent oxidation.

The heat treatment followed wherein a sample was first heated to $1300^\circ C$ at a rate of $10^\circ C/min$ and the temperature then maintained for several hours. The gas was added at 100 ml/min. After the treatment, the sample was cooled to room temperature.

An XRD sample was then prepared to enable analysis of the material structure. XRD measurement was conducted in the range of 20° to 140° of 2-theta, with 0.01° increments per second.

In the second experiment, to compare the interaction layers of $UO_{2.0}$ and UO_{2+x} , a UO_{2+x} disk was reduced using $Ar+4\%H_2$ at $1300^\circ C$ for eight hours. The same heat treatment procedure as above was then carried out.

To analyze the interaction layer and surface, the UO_2 disk and Zry4 were measured using OM.

3. Results and Discussion

3.1 UO_{2+x} - Zry4 interaction

Figure 1 shows the surface of Zry4 in which a Zr metal phase can be seen. The sample was measured using XRD to reveal that the Zry4 is in an α -Zr phase



Fig1. surface of the Zry4 after experiment

Figure 2 shows surface of UO_{2+x} disk. There are two layers. Black part is interaction part. We analyzed the surface using XRD. Fig3 is X-ray diffraction pattern of surface of the UO_{2+x}

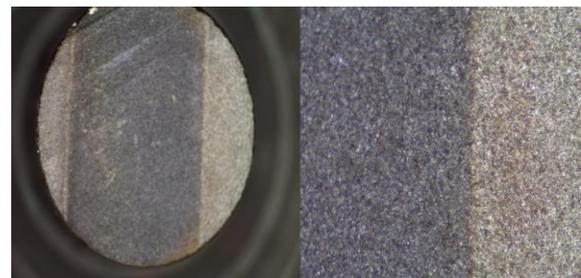


Fig2. surface of the UO_2 disk after Experiment

Figure 3 presents the XRD results in which differences to the starting material can be observed. The UO_2 peak has moved to a higher angle, a shift which is due to the formation of $(U-Zr)O_2$.

The theoretical radii of Zr and U are 0.988 \AA and 1.148 \AA , respectively, meaning that Zr has a smaller radius than U. So, the volume of $(U-Zr)O_2$ decreases as the Zr ratio increases, thereby causing the XRD peak to shift to a higher angle; this also results in a shrinking of the unit cell[4]

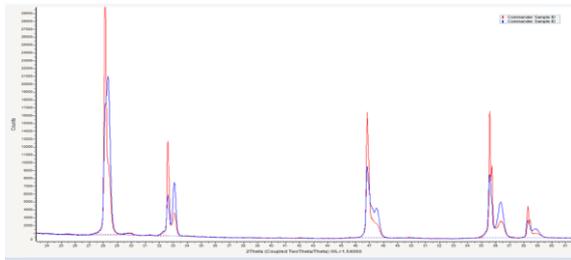


Fig3. X-ray diffraction pattern of Zry4 surface

Figure 4 presents OM images of the Zry4; in terms of phase, the black areas are β -Zr and the white parts are α -Zr. As interaction time increases, the Zr cladding becomes α -Zr rich. The right side of the Zr is the interaction layer which was oxidized by UO_2 during the treatment. At the same time, UO_{2+x} was reduced by the Zr. Above $800^\circ C$, α -Zr transforms to β -Zr, however β -Zr then absorbs the oxygen and transforms to α -Zr. At high temperatures, α -Zr is more brittle than β -Zr and therefore worsens the integrity of the cladding.

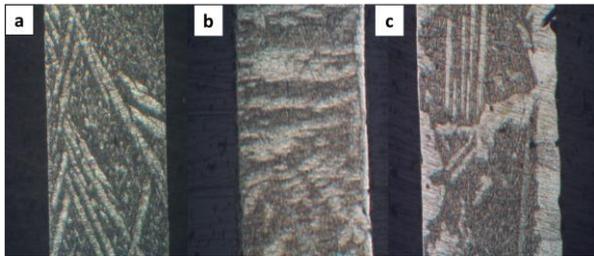


Fig4. OM image of the Zry4 (a)1300°C, Not interaction (c)1300°C, 3h interaction, (d) 1300°C, 5h interaction

3.2 $UO_{2.0}$ - Zry4 interaction

Figure 5 presents OM images after $UO_{2.0}$ - Zry4 interaction at $1300^\circ C$ for two hours. $UO_{2.0}$ that had been reduced from UO_{2+x} was used in this experiment. Unlike our previous experiment, the $UO_{2.0}$ and Zry4 produced a eutectic phase and bonded together, as also reported in an earlier study [1]. As expected, four layers were generated: [α -Zr+(U-Zr)], [(U,Zr)], [α -Zr], and [β -Zr]

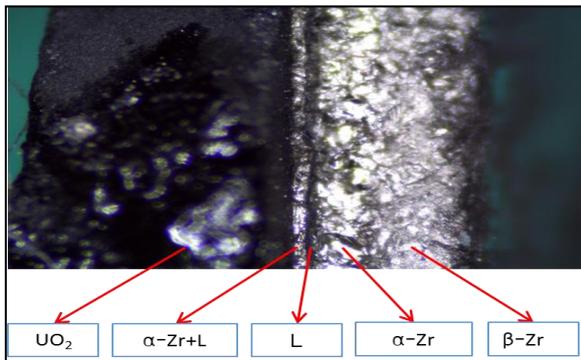


Fig5. $UO_{2.0}$ -Zry4 interaction layer

As illustrated in Quaini et al's ternary phase diagram of the U-Zr-O system [2] (Fig. 6), $UO_{2.0}$ and Zr interact to make the [α -Zr+(U-Zr)] because the Zr reduces the $UO_{2.0}$ to UO_{2-x} . Moreover, the melting point of U is

$1132^\circ C$ meaning that a eutectic phase is produced above that temperature and a U-Zr alloy layer is formed

Figure 6 presents diffusion path of each interaction layers. $UO_{2.0}$ interaction with Zry4 form five layers, its diffusion path are [e-f-g, h-i].

UO_{2+x} interaction with Zry4 form four layers. Its diffusion path are [a-b-c-d]

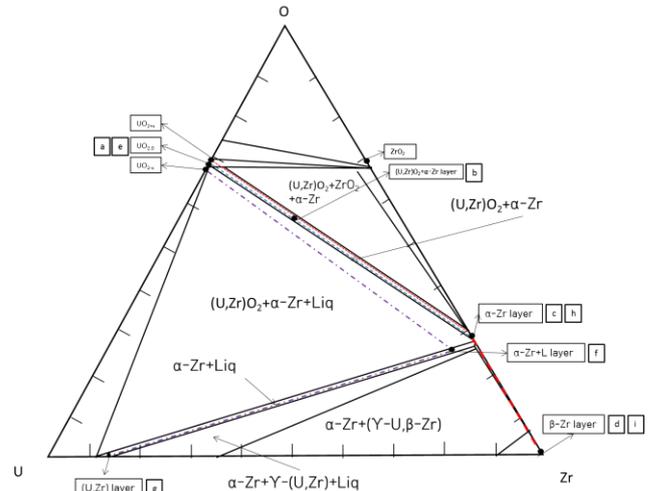


Fig6. U-Zr-O Ternary phase diagram in 1573K [2]

Unlike the model of $UO_{2.0}$ and Zry4 interaction presented in Figure 8, the UO_{2+x} and Zry4 interaction has four layers: [UO_2], [(U-Zr) O_2], [α -Zr], and [β -Zr] (Fig.7). As the interaction time increases at high temperatures, β -Zr becomes α -Zr.

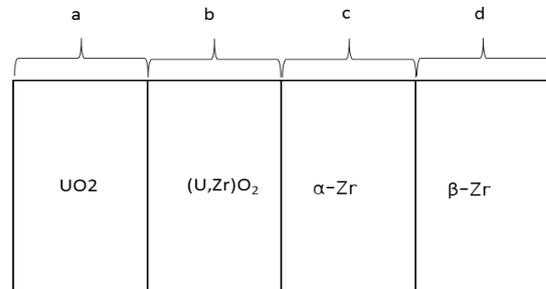


Fig7. Model of UO_{2+x} - Zry4 interaction

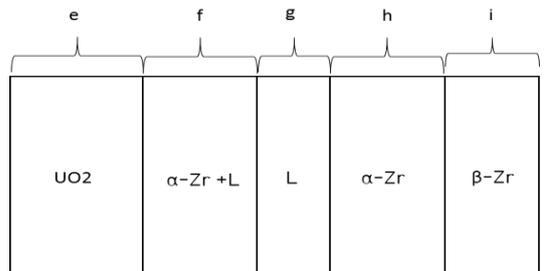


Fig 8. Model of $UO_{2.0}$ - Zry4 interaction[3]

4. Conclusions

UO_2 interaction with Zr cladding above $1200^\circ C$ has been reported to form five layers, namely [UO_2], [α -Zr+(U-Zr)], [(U-Zr)], [α -Zr], and [β -Zr] [1]. However, hyper-stoichiometric UO_2 (UO_{2+x}) forms a different layer

than stoichiometric UO_2 ($\text{UO}_{2.0}$) because UO_{2+x} is more oxidized than $\text{UO}_{2.0}$ and so it is not reduced to UO_{2-x} by interaction with Zr cladding. As a result, it forms an different layer to $\text{UO}_{2.0}$ -Zr cladding

UO_2 produced a (U-Zr) O_2 layer on the outside of the disk because Zr diffuses to the UO_2 side. Therefore, the XRD peak shifted to a higher point and the unit cell shrank.

REFERENCES

- [1] D.R. Olander. The UO_2 -zircaloy chemical interaction. *Journal of Nuclear Materials*. 1983;115:271-285.
- [2] A. Quaini, C. Gueneau, S. Gosse, N. Dupin, B. Sundman, E. Brackx, R. Domenger, M. Kurata, F. Hodaj. Contribution to the thermodynamic description of the corium — The U-Zr-O system. *Journal of Nuclear Materials*. 2018;501:104-131.
- [3] P. Hofmann, C. Politis. The kinetics of the uranium dioxide-zircaloy reactions at high temperatures. *Journal of Nuclear Materials*. 1979;87:375-397.
- [4] R. Perriot, X.-Y. Liu, C.R. Stanek, D.A. Andersson. Diffusion of Zr, Ru, Ce, Y, La, Sr and Ba fission products in UO_2 . *Journal of Nuclear Materials*. 2015;459:90-96.