

CRUD Effect on Zry-4 Oxidation

Yeonseung Kim^{a*}, Kwangheon Park^a

^aDepartment of Nuclear Engineering, Kyunghee University, Kyunggi-do, 446-701

*Corresponding author: specialkys@khu.ac.kr

1. Introduction

CRUD (Chalk River Unidentified Deposits) is formed on the fuel cladding surface under the circulation of corrosion products containing metal ions in the primary circuit of reactors. CRUD is known to form on the boiling region as a deposit due to an abrupt change of solubility of dissolved ions (Fe, Ni, Cr, etc.). CRUD makes a local hot spot and disturbs the cladding's heat transfer resulting in quick corrosion of cladding. And there are several cases of axial offset anomaly (AOA) reported and CRUD is turned out to be the reason [1].

The surface of some spent fuels is covered by CRUD. A long time of exposure to the air is expected during the dry storage condition, and the effect of CRUD on the oxidation of the cladding covered by CRUD is not known yet. We made Zry-4 claddings covered by CRUD, and analyzed the effect of CRUD on the air oxidation of Zry-4.

2. Methods and Results

2.1 Simulated CRUD formation

2.1.1 Specimen

We used Zry-4 tube as received condition from the supplier. The length of the specimen was about 500 mm, and its surface was cleaned by acetone.

2.1.2 Simulated Primary Coolant

Table 1 shows the chemical composition (%) of simulated primary coolant. The simulated primary coolant consisted of boric acid (1000 ppm) and lithium hydroxide (3 ppm) [2].

Table 1. Chemical composition of specimen

Metal	Fe	Zn	Cr	Ni	Co
concentration (ppm)	8.56	1.00	0.79	0.45	0.08
(wt %)	(78.7)	(9.2)	(7.3)	(4.1)	(0.7)

2.1.3 Apparatus and Method

Fig. 1 shows the apparatus for the fuel crud formation. After the specimen (Zry-4 tube) was inserted into the furnace and connected to the system, the simulated primary coolant was circulated through the system. High pressure (15MPa) was maintained by a water pump. The temperature of the tube was controlled by an electronic

heater outside. CRUD started form on the inner side of the tube.

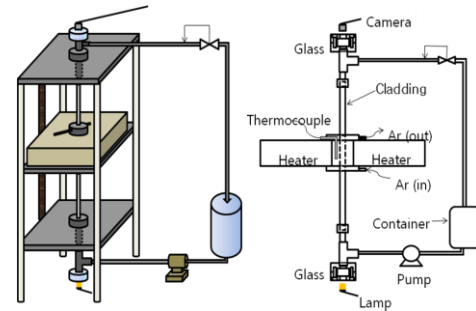


Fig. 1. Apparatus of the crud sampling system

Ar gas flowed through between the heater and the cladding in order to prevent cladding oxidation. The temperature of the tube was 350 °C at the center.

2.1.4 Results of the CRUD Formation Experiments

After one week of the CRUD formation experiment, a video borescope was used to get the surface image of simulated CRUD. Fig. 2 shows the images of the specimen taken. The color faded into yellow to brown as approaching to the center region. Most CRUD was created in the hot zone, since corrosion products have a tendency to deposit (Fe, Ni, Cr, etc.) on the boiling region [3].

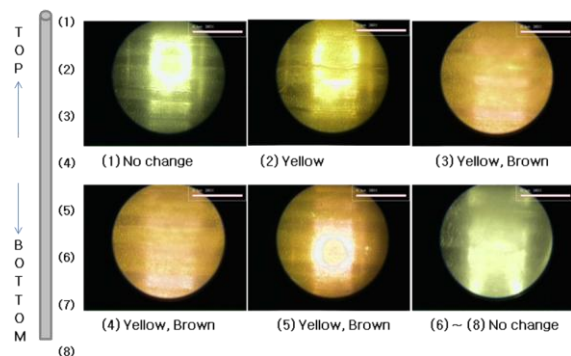


Fig. 2. Video borescope image of the simulated CRUD

2.2 High Temperature Oxidation Behavior

2.2.1 Oxidation Apparatus and Experiments

The cladding tube containing CRUD was cut to the height of 10 mm, then ground, polished and cleaned and used for the specimens. For comparison, specimens of normal Zry-4 were also prepared. The apparatus for high temperature oxidation was made as shown in Fig. 3.

An electronic heater was able to move up and down. The heater was moved up to the position of the specimen after oxidation temperature was reached. Helium was supplied to the microbalance for the protection of possible damage. The weight gain was measured and recorded continuously to a PC connected to the microbalance. The accuracy of the measurement was about $10\mu\text{g}$. The target temperature range was from $700\text{-}900^\circ\text{C}$, and the oxidation time was about 2000sec.

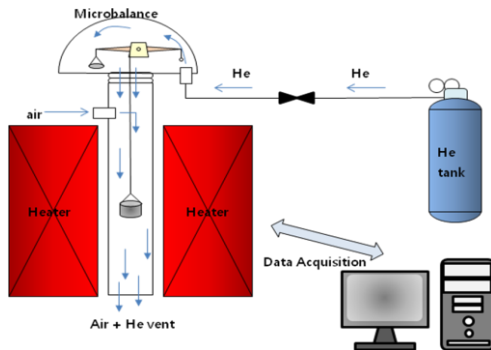


Fig. 3. Apparatus for high temperature oxidation in the air

2.2.2 Results of the Oxidation Experiments

Fig. 4 shows the final weight gain of the specimens under the one atmosphere air. The specimens with CRUD gained more weight than normal tube specimens.

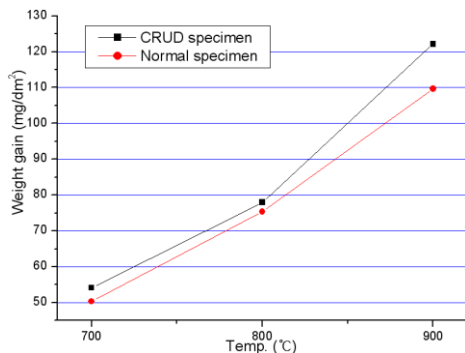


Fig. 4. Weight gain of Zry-4 under the one atmosphere air.

Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) were used to observe the microstructures of the specimen oxide layer (Fig.5). The CRUD layer on the oxide became a porous layer of the oxidized CRUD. The oxide layer formed under CRUD looks thicker than that of the normal cladding. The reason for the thicker oxide formed under the CRUD is not known and still under the analysis. The CRUD may destabilize the initial oxide formation. Fig.6 shows the weight gain curve at 900°C during the air oxidation. At the stabilized zone oxidation kinetics follow a parabolic rate law approximately (slope=0.42). Initial slopes before the stabilization are clearly different between two specimens. The oxidation of CRUD on the surface may be a reason for the difference. However, the oxide formed under the CRUD was thicker.

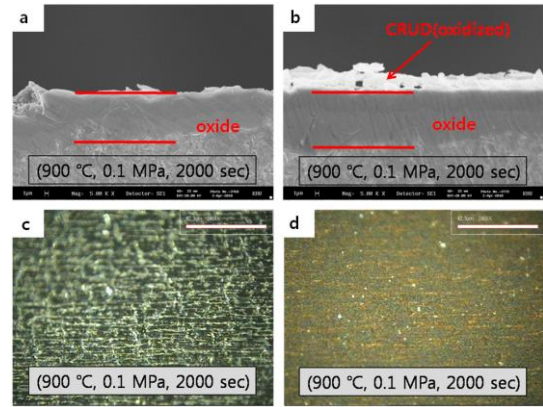


Fig. 5. SEM image and OM image

- (a) SEM image of normal specimen (oxide layer).
- (b) SEM image of CRUD specimen (oxide layer).
- (c) OM image of normal specimen (surface of specimen).
- (d) OM image of CRUD specimen (surface of specimen).

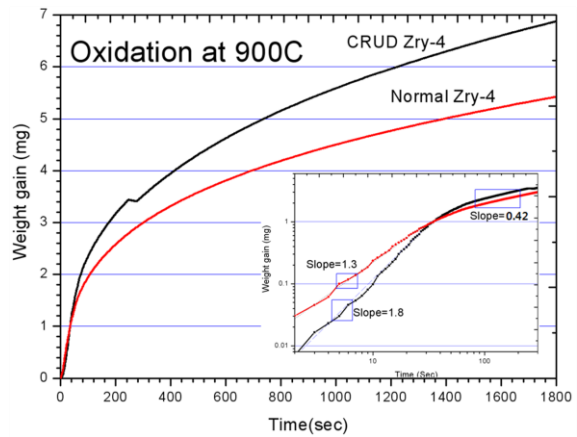


Fig.6. Oxidation kinetics at 900°C

3. Conclusions

CRUD formation experiments were done and Zry-4 tube specimens covered by simulated CRUD inside the tube were prepared. The color of CRUD looked yellowish brown. Air-oxidation tests were done using both CRUD deposited and normal Zry-4 tubes. CRUD deposited tubes were oxidized more than normal ones (5-10%). Microscopic analyses indicated that oxide thickness was bigger in the case of specimens with CRUD. The reason for the thicker oxide formation is still under the analysis. The initial oxidation kinetics seemed to be slight different, and the oxidation rate of CRUD deposited specimen was the higher.

REFERENCES

- [1] J. W. Yeon, Y. J. Jung, and S. I. Pyun, Deposition behavior of corrosion products on the Zircaloy heat transfer surface, *Journal of Nuclear Materials* 354, p.163-170, 2006.
- [2] K. S. Kim, H. J. Lee, D. W. Kang, and S. Inoue, Synthesis of simulated crud for development of decontaminating agents, *Nuclear Engineering and Design* 223, p.329-337, 2003.
- [3] K. S. Jung, and B. K. Hong, Survey of Water Chemistry and Corrosion of NPP, KAERI/AR-804/2008.