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CRUD deposition experiment in simulated PWR primary water chemistry

Yunju Lee[a], Seungchang Yoo[a], Byung Gi Park[b], Ji Hyun Kim [a*]

[a] *Department of Nuclear Engineering, School of Mechanical, Aerospace, and Nuclear Engineering, Ulsan National Institute of Science and Technology, 50 UNIST-gil, Ulsan, 44919*
[b]*Department of Energy & Environmental Engineering, Soonchunhyang University, 22, Soonchunhyang-ro, Asan, Chungcheongnam-do 31538, Republic of Korea*
[*]*Corresponding author: kimjh@unist.ac.kr*

1. Introduction

As commercialized power reactor, Pressurized Water Reactor (PWR) has been operated for a long time. To enhance economic efficiency, the burn-ups of nuclear fuel have been increased. In the reactor core, some unexpected power shifts, which shows negative axial offset from prediction, have been observed. This phenomenon is called by AOA (Axial offset Anomaly) and it seems to be caused by deposits on the upper side of fuel cladding surface which is called CRUD (Chalk River Unidentified Deposit, or Corrosion Related Unidentified Deposit).[1]

This kind of problem is caused by combination of thermohydraulic and corrosion phenomenon. From previous studies it is found that AOA occurred PWR have common characteristics, some degree of nucleate boiling on the fuel cladding, this indicates that the deposition of corrosion products by nucleate boiling is a root cause of AOA phenomenon.[1,2]

CRUD may cause another problem concerned with corrosion mechanism. Irregularly deposited CRUD makes temperature gradient in the cladding surface and it induce localized corrosion of cladding tube. CILC (CRUD Induced Localized Corrosion) can provoke significant safety problem for cladding tube. According to previous studies it was found that CRUD is composed of corrosion products of Ni and Fe, such as nickel metal (Ni), nickel oxide (NiO), iron metal, magnetite (Fe_3O_4), nickel ferrite ($NiFe_2O_4$).[1,3] Ni and small amount of Co are activated and the total amount of radiolysis on the fuel cladding could be increased.

By predicting the CRUD deposition and its property and by providing the data to thermohydraulic code and neutron transfer code, influence of CRUD such as occurrence of AOA and CILC and an increase of radioactive substance, can be estimated. To develop a water chemistry code, which can predict the CRUD deposition, CRUD deposition experiments have been conducted by many research groups to investigate the properties of CRUD.[4,5] In the research project of this paper, to characterize the CRUD in accordance with its formation condition, CRUD deposition experiment would be performed with variation of heat flux at cladding, variation of corrosion product ion concentration, and time variation.

In this paper, the first experiment which is conducted for low heat flux condition and high metal ion concentration has been conducted. Shape information of the specimen is characterized by Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) with Focused Ion Beam (FIB) instrument. And its chemical composition is investigated by Electron Dispersed Spectroscopy (EDS). To reveal the axial characteristic of the CRUD specimen, the analysis was conducted along axial direction of the specimen.

2. Experimental

2.1 Experimental condition and procedure

CRUD deposition experiment was conducted to investigate the characteristic of CRUD according to the thermohydraulic condition and water chemistry condition. As mentioned, three major conditions should be satisfied for CRUD deposition, sub-cooled boiling at cladding surface, existence of corrosion product in the primary water, and boron and lithium ion in the primary water.

Table. 1 Experimental conditions of CRUD deposition experiment with low hear flux condition.

Effective full power day [day]	7
Length of specimen [mm]	300
Outer diameter of specimen [mm]	9.5
Inner diameter of specimen [mm]	8.34
Pressure [MPa]	15.5
Average mass flux [kg/s]	0.01
Surface temperature of specimen [℃]	350.4
Heat flux at specimen [kW/m^2]	46
Average coolant temperature [℃]	318 ~ 330
DH concentration [ppm]	2.7
DO concentration [ppb]	~ < 5
pH [ppm]	6.9 ~ 7.4
Boron concentration [ppm]	1200
Lithium concentration [ppm]	2.2
Nickel concentration [ppm]	25
Iron concentration [ppm]	12

Because the CRUD deposition behavior occurs at upper span of the fuel assembly, the experimental conditions was set to simulate the top span of fuel assembly of OPR1000. Heat flux of a fuel cladding is limited to 1 MW/m^2, however, in this paper, CRUD deposition experiment was conducted with lower heat flux condition. The experiments for higher heat flux condition will be done later. Experimental conditions of low heat flux experiment are summarized in Table.1.

As mentioned, to simulate top span of a fuel cladding, 300 mm of Zr-Nb-Sn alloy tube is used for fuel cladding specimen. Using direct current heating method, heat flux condition on surface of the specimen was satisfied. The corrosion product dissolved in primary water, is simulated by metal ions such as nickel and iron, which are injected with nickel acetate and Fe Ethylenediaminetetraacetic acid (EDTA). To accelerate the CRUD deposition, concentrated metal ion solutions were used. The CRUD deposition experiments were conducted for 7 days.

2.2 Analysis strategy

Visual inspection was conducted for the entire specimen to observe macroscopic characteristic of CRUD deposition behavior. OM images were taken to observe surface of the specimen in macro-scale.

After the visual inspection, microscopic observation was conducted with FIB-SEM instrument. To investigate the axial characteristic of the CRUD, the specimen is cut in three pieces in axial direction (Top, Middle, Bottom in Fig. 1) and SEM was conducted for each specimen.

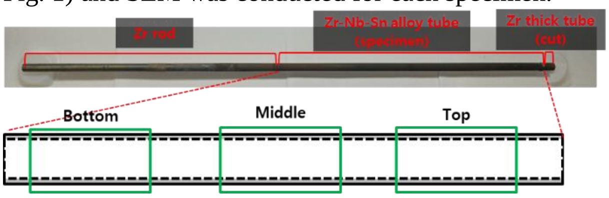

Fig. 1 Schematic diagram of specimen sectioning plan.

SEM was performed for both surface and cross section of the specimen. Cross section planes were trimmed by FIB and EDS was conducted for cross section plane of each specimen.

3. Result & Discussion

3.1 Visual inspection for entire specimen

Visual inspection was performed with the unaided eye and OM instrument to observe the surface morphology in macro-scale. From the photograph of the specimen (Fig. 2) it can be known that dark and brown colored porous deposits were formed on the surface of the specimen. The deposits become pale as the axial position goes bottom. However, there was no difference along azimuthal direction of the specimen.

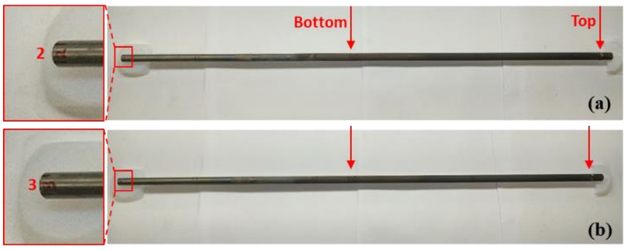

Fig. 2 Photograph of the CRUD deposited sample (a) for #2 plane. (b) #3 plane (90º turned in azimuthal direction from #2). The end of Zr-Nb-Sn tube is indicated with red arrow. Left side of the tube is located at bottom when the specimen loaded.

From OM images in Fig 3, it can be identified that some chimney-like structure is formed on the surface. The pore size was too small to measure its exact size with OM images, but it is obvious that its diameter is much smaller than a previous research, which is conducted by Westinghouse research center.[3]

Fig. 3 OM image of the surface of specimen.

3.2 Top specimen

SEM surface image was taken from Top specimen to check its morphology. As shown in OM image, chimney-like structure was also found from the SEM surface images in Fig.4. Because most of large surface chimneys (or pore) have small chimneys (or pores) in it, it is hard to define a chimney size and shape.

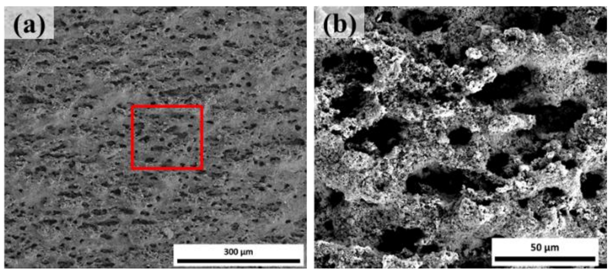

Fig. 4 SEM surface image of Top specimen. A small region of (a) which indicated with red box is magnified and showed in (b).

To observe the shape of CRUD layer in radial direction cross section of the specimen is made by FIB in perpendicular with axial direction of tube. The SEM image of Cross section plane is obtained in Fig. 5 and point EDS results is summarized in Table 2. The cross-section image show that CRUD is formed on the rigid ZrO2 layer. The maximum thickness of the CRUD in the FIB spot of Top specimen was 64.34 μm and the minimum thickness is 44.21 μm. Average CRUD thickness is 56.82 μm with standard deviation 6.07.

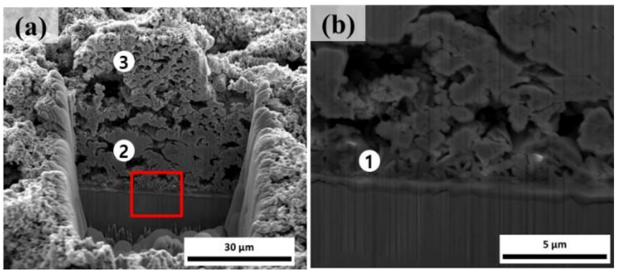

Fig. 5 SEM cross section image of Top specimen. A red-boxed region in (a) is magnified and shown in (b).

Table. 2 Point EDS analysis of the points in Fig. 5(b) in a.t.%

Point	O	Fe	Ni	Zr	Ni/Fe ratio
1	64.2	9.9	4.5	21.4	0.46
2	55.1	22.3	12.6	10.0	0.57
3	64.1	21.7	11.3	2.9	0.52

CRUD particle size is getting smaller as far from the heated surface. It seems to be caused by temperature gradient of nano-particle along the radial direction. It seems like needle-like structure are formed on the bottom layer of the CRUD. (Fig. 5 (b)) From the point EDS, it is known that Ni/Fe ratio is about 0.5 which means Nickel ferrite deposited majorly. Ni/Fe ratio was slightly increase from cladding to outer surface, however any noticeable change was not found.

3.3 Middle specimen

SEM and EDS analysis were also conducted for Middle specimen. Surface region become smooth as the position go to the bottom region. (Fig. 7) As like surface image no chimney-like structure are found on the smooth surface. Cracks are found on smooth surface and inside the crack, CRUD is deposited, and it seems like to have chimney-like structure.

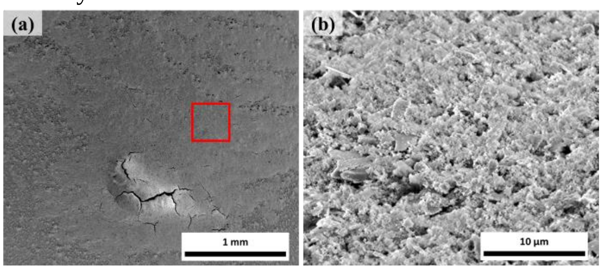

Fig. 6 SEM surface image of Bottom specimen. A red-boxed region in (a) is magnified and shown in (b).

From the cross-section image in Fig. 7, it was found that the thickness of CRUD is much thinner than top region of the specimen. Average thickness is 21.51 μm with standard deviation 0.889. Nano-scale particles are deposited, near outer surface region, and slightly larger particles are deposited near CRUD/ZrO_2 interface. It seems like deposit particles are agglomerate in heated surface as like in the Top specimen, whereas degree of agglomeration is much smaller at Middle specimen so that Middle specimen seems to have much denser than Top specimen. This dense CRUD may cause the crack, which is formed on the surface of the specimen (Fig. 6)

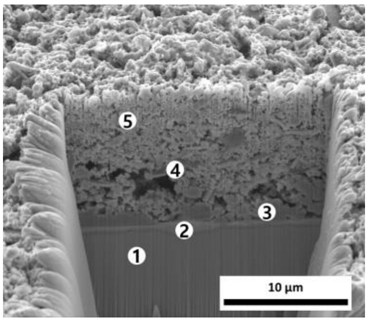

Fig. 7 SEM cross section image of Middle specimen.

Table. 3 Point EDS analysis of the points in Fig. 7 in a.t.%

Point	O	Fe	Ni	Zr	Ni/Fe ratio
1	46.44	4.47	1.72	47.37	-
2	47.1	3.18	1.03	48.69	-
3	65.71	4.44	3.45	26.36	0.78
4	62.43	17.38	10.99	9.2	0.63
5	73.02	15.95	8.23	2.52	0.52

From the EDS results which is shown in Table 3, the Ni/Fe ratio is abruptly decreased from CRUD/ZrO_2 surface to outer surface of CRUD. The large particles which is deposited near CRUD/ZrO_2 surface, seems to nickel containing particles.

3.4 Bottom specimen

For bottom specimen, SEM and EDS analysis were also performed. From the surface image in Fig. 8, the CRUD was deposited thinly on the surface, and the partially deposited part was observed. Predominantly chimney was observed in some of the partially highly deposited CRUD. As the surface temperature of the specimen was lower than that of the upper and middle parts, CRUD is deposited less than Middle or Top specimen. The average CRUD thickness at the cross-section was measured as 10.49 μm (σ = 4.605). Unlike the Top and Middle specimens, no change in the size of the crud particle was observed in the radial direction, but nano-sized crud particles were deposited near the outer surface. In the SEM cross-sectional image, the Ni ratio is high in the particles that appear to be agglomerated at the center.

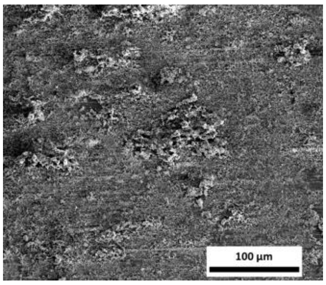

Fig. 8 SEM surface image of Bottom specimen.

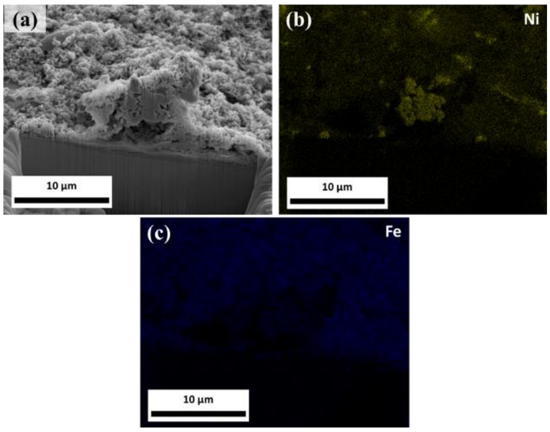

Fig. 9 (a) SEM cross section image of Bottom specimen. And its EDS mapping image for (b) nickel and (c) iron.

5. Conclusions

With the FIB-SEM and EDS analysis, characteristic of CRUD along axial direction of cladding specimen is investigated. At the top of the specimen, where temperature of specimen and coolant is high, have chimney structured CRUD whereas CRUD which formed in middle region was dense. The thickness of CRUD have its maximum value at the top of specimen and become thinner as goes bottom. The Ni/Fe ratio of the CRUD is decreased along axial direction. Agglomerated nickel particles are found on the bottom of the specimen and some are found on the middle of the specimen. Whereas Ni/Fe ratio of top region was kept about 0.5 which means that nickel ferrite is dominantly formed on the top of the specimen.

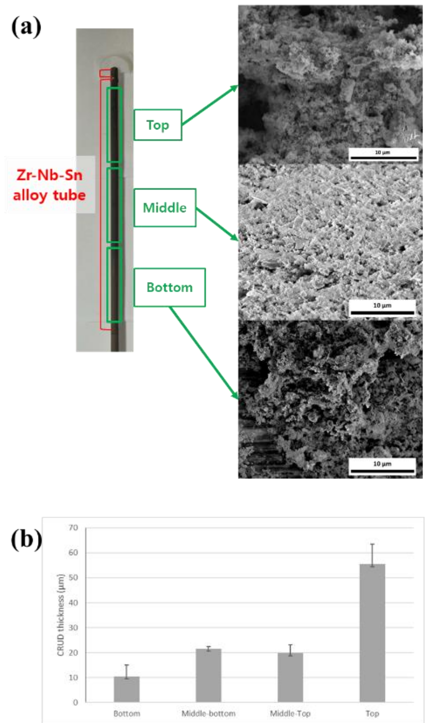

Fig. 10 (a) Surface morphology and (b) CRUD thickness along axial direction of the specimen.

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