

Effect of Corrosion Product Concentration on Structure and Thermal Property of Fuel CRUD in PWR

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1. Introduction

In a Nuclear Power Plant (NPP), the formation of Corrosion Product Related Deposit (CRUD), also known as Chalk River Unidentified Deposits, occurs due to sub-cooled boiling on the upper part of fuel cladding. This phenomenon causes serious safety and economic issues associated with boron accumulation and the radioactivation of the deposits themselves [1-4]. The deposition of CRUD and boron accumulation are affected by the chemical and thermal-hydraulic behavior of water in the vicinity of the fuel cladding surface [5]. Therefore, it is crucial to investigate the mechanism of CRUD deposition and its effects on the chemical and thermal-hydraulic conditions to accurately predict the impact of CRUD deposition. Although the thickness and structure of CRUD are known to be dependent on the heat flux conditions of the fuel cladding surface and the metal ion concentration of the coolant, limited research has been conducted on the microstructure changes of CRUD under different metal ion conditions.

To address this gap, an experimental facility was established to investigate CRUD deposition on fuel cladding under various water chemistry conditions in a simulated Pressurized Water Reactor (PWR) primary water. In a previous study, the effect of heat flux on CRUD structure and chemistry was examined for high metal ion concentration conditions. In this study, we conducted a CRUD deposition experiment for two different metal ion concentrations to investigate the effect of metal ion concentration conditions on CRUD formation. The specimens were observed using a Scanning Electron Microscopy (SEM) with a Focused Ion Beam (FIB) instrument. The chemistry and microstructure of the CRUD specimens were examined using Energy Dispersive X-ray Spectroscopy (EDS).

2. Experimental Methods

2.1. Experimental condition

In order to accurately simulate the CRUD deposition at the reactor core, three major conditions must be satisfied, namely, the existence of corrosion products in the primary water, sub-cooled boiling at the cladding surface, and the presence of dissolved boron and lithium species in the primary water. Corrosion products, which are known to be a major source of CRUD, are formed by the structural materials of the primary coolant system. In Pressurized Water Reactors (PWRs), approximately 80%

of the primary coolant system surface is composed of nickel alloys, while the rest is typically made of stainless steel. Taking into account the corrosion rate and surface composition of the alloys, the dissolved Ni/Fe ion rate is calculated to be 2, which is in agreement with the chemical analysis results of Halden reactors.

To simulate the corrosion product, metal ions such as nickel and iron are injected using nickel acetate and Fe Ethylenediaminetetraacetic acid (EDTA). In order to accelerate the CRUD deposition, concentrated metal ion solutions are used. The appropriate Ni and Fe ion concentrations are assumed to be 100 ppb and 50 ppb, respectively, as Ni and Fe ion concentrations are typically limited to 100 ppb in PWR primary coolant. To simulate 1 cycle (18 months) of NPP operation in 7 days of experiment, a Ni solution of 12.5 ppm and an Fe solution of 6 ppm are prepared. To investigate the effect of metal ion concentration on the formation of CRUD, the CRUD deposition experiment is also conducted using solutions that are two times more concentrated with metal ions.

The degree of sub-cooled boiling at the fuel cladding specimen is controlled by adjusting the heat flux condition. As the CRUD deposition behavior occurs at the upper span of the fuel assembly, the experimental conditions are set to simulate the top span of the fuel assembly of OPR1000. The heat flux of the top span fuel cladding is low (approximately 150 kW/m²), while the coolant temperature of a top span fuel cladding is high (approximately 320°C). Other chemical and thermal conditions are set to simulate PWR primary water. The experimental conditions are summarized in **Table 1**.

Table 1. Experimental conditions of CRUD deposition experiment.

Experimental condition	Low Metal Ion concentration	High Metal Ion concentration
Nickel concentration [ppm]	12.5	25
Iron concentration [ppm]	6	12
Heat flux at specimen [kW/m ²]	150	150
Surface temperature of specimen [°C]	349 ~ 351	357 ~ 365
Average coolant temperature [°C]	318 ~ 330	310 ~ 315
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	

DH concentration [ppm]	2.7
DO concentration [ppb]	~ < 5
pH [ppm]	6.9 ~ 7.4
Boron concentration [ppm]	1200
Lithium concentration [ppm]	2.2

To conduct in-situ surface temperature measurement, a thermocouple is affixed to the inner surface of the specimen. The test section autoclave is situated within the test section loop, thereby allowing for the creation of high-pressure, high-temperature, and high-flow-rate conditions. The cladding specimen was installed within the test section autoclave by penetrating the autoclave. This installation method enables the specimen to be connected to an electrode

2.2. Analysis strategy

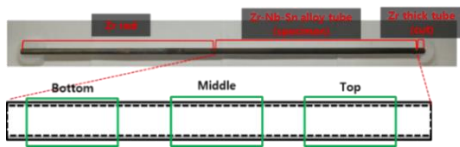


Figure 1. Schematic diagram of a fuel cladding specimen.

A visual inspection of the entire specimen was performed to observe the macroscopic characteristics of the CRUD deposition behavior. Optical microscopy (OM) images were captured to observe the surface of the specimen in the macro-scale. Following this initial inspection, a microscopic observation was conducted using a FIB-SEM instrument. To investigate the axial characteristics of the CRUD, the specimen was cut into three pieces in the axial direction (top, middle, and bottom as shown in Figure 1) and SEM was conducted for each specimen.

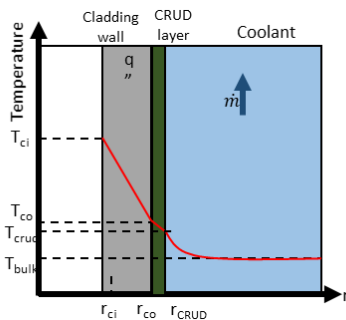


Figure 2. Schematic diagram of temperature change near cladding wall.

$$k_{CRUD} = \frac{q'' \pi D_{co}}{A_{crossL}} \cdot \frac{1}{4(T_{co} - T_{CRUD})} \left[2r_{co}^2 \ln\left(\frac{r_{co}}{r_{CRUD}}\right) + (r_{CRUD}^2 - r_{co}^2) \right] \quad (1)$$

Throughout the experiment, the cladding surface temperature was observed to increase following metal ion injection, suggesting the formation of a CRUD layer

which can act as a heat transfer resistance. In this study, the effective thermal conductivity of the CRUD layer was determined by calculating the temperature difference before and after its formation. This was achieved by assuming that the bulk coolant temperature and convective heat transfer coefficient of the cladding/coolant interface or CRUD/coolant interface were equal before and after the deposition of the CRUD layer. The effective thermal conductivity was then calculated using Equation 1.

3. Results and discussion

3.1. Structural and chemical analysis of CRUD layer

SEM surface images were captured from the top specimen in order to investigate the morphology of the CRUD layer, including particle size, particle type, porosity, and chimney structures (as illustrated in Figure 3). The analysis of the SEM surface image showed that the majority of the CRUD layer in both specimens was composed of particles with dimensions of only a few nanometers, and only a small amount of fetal-like structures were observed. Primitive chimney structures were observed in the CRUD layer formed at low metal ion concentrations (Figure 3(a)), whereas fully developed chimney structures were observed in the CRUD layer formed at high metal ion concentrations (Figure 3(b)).

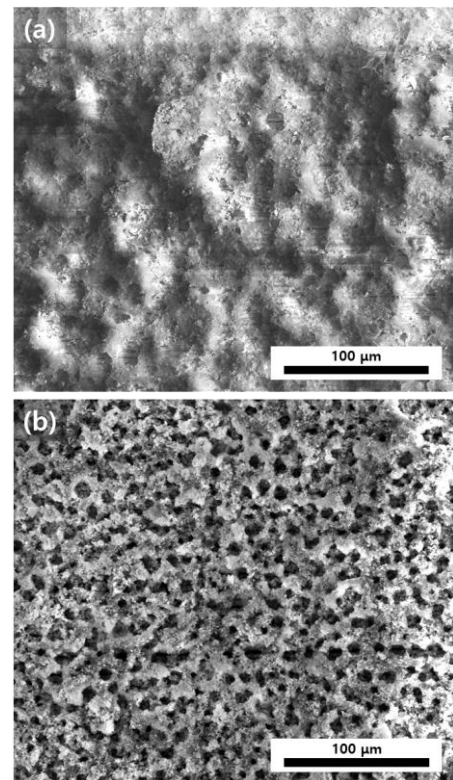


Figure 3. Surface image of CRUD layer which formed in (a) low metal ion concentration and (b) high metal ion concentration.

The structural characteristics of the chimney and CRUD layer were examined using a dual beam FIB-SEM. A cross-section of each specimen was fabricated by FIB, perpendicular to the axial direction of the tube. Point EDS was measured in the radial direction, and the EDS location was indicated within the CRUD thickness (as shown in Figure 4 and Figure 5).

Both specimens exhibited a tortuous chimney structure that extended from the cladding surface to the CRUD surface. The structural features such as particle size, chimney size, and porosity were similar in both specimens, except for the thickness. However, a discernible difference was observed in the chemical compositions of the inner CRUD layer of each specimen. Specifically, while the Ni/Fe ratio of the high metal ion concentration specimen increased outward and reached 2, the Ni/Fe ratio of the low metal ion concentration specimen remained constant at 2.

According to a previous study that summarized numerous analyses of CRUD formation on PWR fuel cladding, it was found that a Ni-rich CRUD layer forms on the cladding surface exposed to more severe temperature conditions. [2,3]

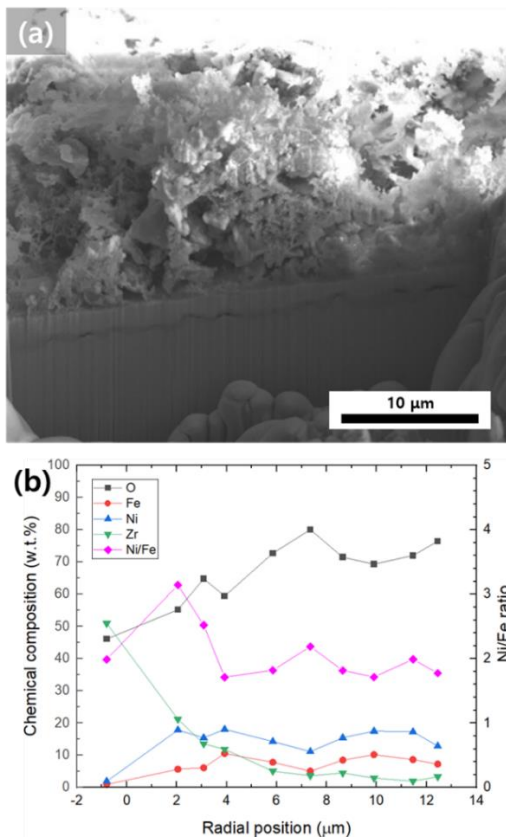


Figure 4. (a) Cross section image and (b) chemical composition of CRUD layer, which formed in low metal ion concentration.

The obtained cross-sectional image revealed the formation of CRUD layer on the rigid ZrO₂ layer. The average thicknesses of both the Zr oxide and CRUD layer

at the FIB spot of the top region were reported in Table 2. It was observed that the Zr oxide layer was thicker and rougher in the specimen with lower metal ion concentration, which suggests that this specimen was exposed to more oxidizing conditions compared to the one with higher metal ion concentration.

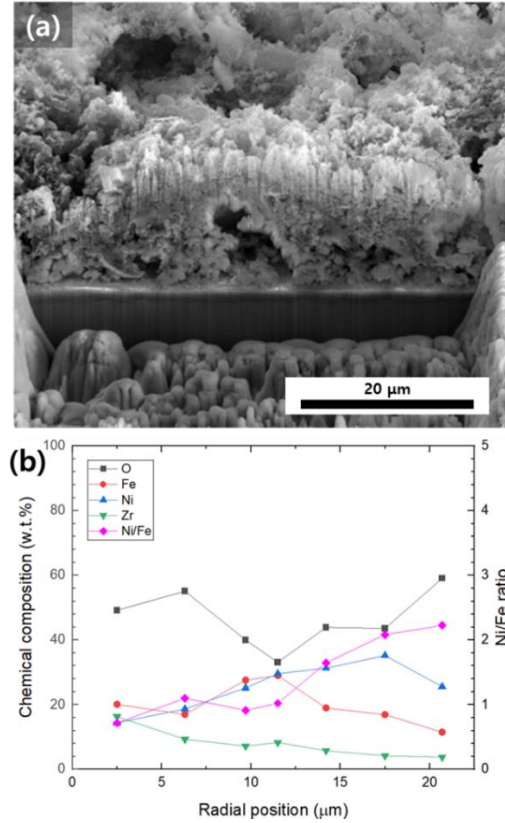


Figure 5. (a) Cross section image and (b) chemical composition of CRUD layer, which formed in high metal ion concentration.

Based on the observation that the low metal ion concentration specimen had a higher Ni/Fe ratio and a thicker oxide layer, it can be concluded that the temperature at the CRUD/cladding interface was higher in this specimen. However, it should be noted that despite this inference, the high metal ion concentration specimen actually had a thicker CRUD layer.

Table 2. Thickness of Crud and Zr oxide

Thickness	Low Metal Ion concentration	High Metal Ion concentration
Zr oxide	2.24μm (σ=0.547)	1.69μm (σ=0.176)
Crud	11.2μm (σ=4.55)	19.1μm (σ=3.16)

3.2 Effective thermal conductivity of CRUD layer

The effective thermal conductivity of the CRUD layer was determined by calculating the surface temperature difference before and after the CRUD deposition

experiment (as presented in Table 3). Although the CRUD layer was much thicker at high metal ion concentration, the effective thermal conductivity of the CRUD was lower. This observation can be attributed to the different stages of chimney structure development in each specimen. The chimney diameter was similar in both specimens, but the chimney length, which is proportional to the thickness of the CRUD layer, was much shorter in the low metal ion concentration specimen.

It is well known that chimney structures promote heat transfer between the cladding and coolant by initiating Wick boiling [4]. As short chimney structures are less favorable for generating Wick boiling, the effective thermal conductivity of the CRUD layer could be lower at the low metal ion concentration specimen, which has more primitive chimney structures.

Table 3. Cladding surface temperature change and calculated thermal conductivity of CRUD

	Low Metal Ion concentration	High Metal Ion concentration
Cladding surface temperature change after CRUD deposition	3.4 °C	2.4 °C
Calculated effective thermal conductivity	0.00561 W/m-K	0.0224 W/m-K

4. Conclusions

Simulated CRUD deposition experiments were conducted with different metal ion concentrations to investigate the effect of corrosion product concentration on CRUD deposition and thermal conductivity. The specimens were analyzed using SEM and EDS to identify the relationship between thermal conductivity and CRUD structure. The effective thermal conductivity of CRUD was calculated using surface temperature difference before and after the experiment. The results showed that effective thermal conductivity of CRUD was lower at low metal ion concentration despite its thinner thickness, and developed chimney structure could promote heat transfer in CRUD far more by actuating Wick boiling behavior than primitive chimney structure. These findings could contribute to better understanding of heat transfer behavior in PWR fuel cladding during operation.

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