Characterization of Corrosion Product Deposition on Fuel Cladding under Boron-Free Coolant Conditions

Junhyuk Jeong, Yunju Lee and Ji Hyun Kim*
Department of Nuclear Engineering, College of Engineering,
Ulsan National Institute of Science and Technology (UNIST)
**Corresponding author: kimjh@unist.ac.kr*

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1. Introduction

During nuclear reactor operation, corrosion products known as CRUD (Chalk River Unidentified Deposits) are deposited on the surface of fuel cladding, acting as a critical factor that influences fuel integrity and thermohydraulic performance. CRUD is primarily formed through nucleate boiling at the cladding surface and the precipitation of metallic ions in the coolant.[1] In i-SMR environments, characterized by high temperature, high pressure, and fast coolant flow, CRUD formation and cladding corrosion occur simultaneously in a complex manner. These processes are highly sensitive to the coolant water chemistry conditions, which determine the solubility of metallic ions, redox states, and precipitation pathways. Such conditions ultimately affect the composition and deposition location of CRUD, leading to the accumulation of radioactive corrosion products, degradation of heat transfer efficiency, and localized corrosion. In particular, nickel and iron species deposited on the cladding surface can exist in multiple phases such as nickel ferrite ($NiFe_2O_4$), nickel oxide (NiO), metallic nickel, magnetite (Fe_3O_4), and metallic iron.[2] Their thermodynamic stability and dissolution behavior vary with hydrogen concentration and pH, resulting in significant changes in CRUD morphology, thickness, composition, and degradation patterns, which in turn impact cladding corrosion characteristics.[3,4] In this study, experiments simulating i-SMR operating conditions were conducted to evaluate CRUD deposition behavior and its associated effects on fuel cladding corrosion.

2. Methods and Results

Preliminary experiments conducted under the KOH-pH6.9-DH25-168h condition revealed that, as shown in Figure 1, a brownish CRUD layer was uniformly deposited on the cladding surface. The CRUD was more prominently formed at the upper region of the cladding, where the coolant temperature was relatively higher, corresponding to the location of intensive subcooled boiling. Accordingly, the specimen was sectioned at the 50 mm position for detailed characterization and analysis.

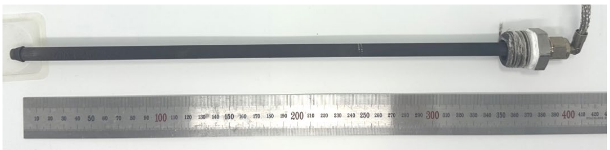

Fig. 1. Zirconium cladding specimen mounted on a cartridge heater

2.1 SEM surface analysis results of KOH-pH6.9-DH25-168h

SEM observations revealed that CRUD was uniformly formed across the entire surface of the fuel cladding, with chimney-like porous structures being clearly identified. The surface morphology indicated the presence of polygonal spinel-type nickel ferrite ($NiFe_2O_4$) particles, along with acicular nickel oxide (NiO) phases. In addition, the CRUD layer was predominantly composed of granular particles, consisting of very fine nanoparticles on the order of a few nanometers together with larger particles of approximately 1–3 μm in size. These findings confirm that the CRUD exhibits a heterogeneous microstructure with distinct particle morphologies and interconnected porous features, which are characteristic of deposition under the KOH-pH6.9-DH25-168h condition.

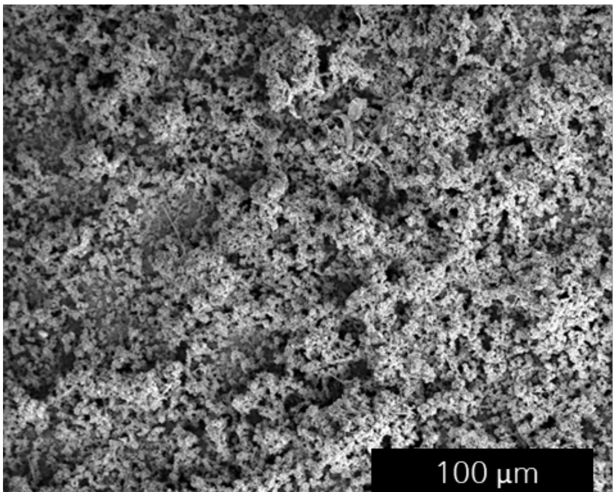

Fig. 2. Surface SEM images of CRUD layer

2.2 SEM cross-sectional analysis of KOH-pH6.9-DH25-168h

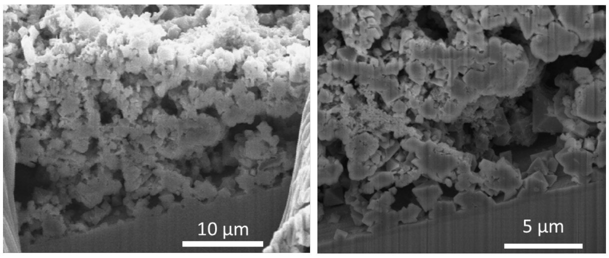

Fig. 3. Cross sectional SEM image of CRUD layer

Cross-sectional SEM analysis revealed that the chimney structures extended through the CRUD layer and were directly connected to the cladding surface. At the CRUD/oxide interface, wide porous regions were observed, whereas the upper regions closer to the surface exhibited a relatively denser morphology. A gradual decrease in particle size was also identified along the axial direction moving away from the cladding surface, indicating a particle refinement trend within the CRUD layer. The microstructure was predominantly composed of granular particles, and it was noted that particles located near the CRUD/oxide interface were relatively larger compared to those in the surface region. These observations collectively demonstrate that the CRUD exhibits a heterogeneous thickness profile with distinct porosity and particle size gradients, reflecting the interplay between deposition, growth, and consolidation processes under the KOH-pH6.9-DH25-168h condition.

2.3 EDS cross-sectional analysis of KOH-pH6.9-DH25-168h

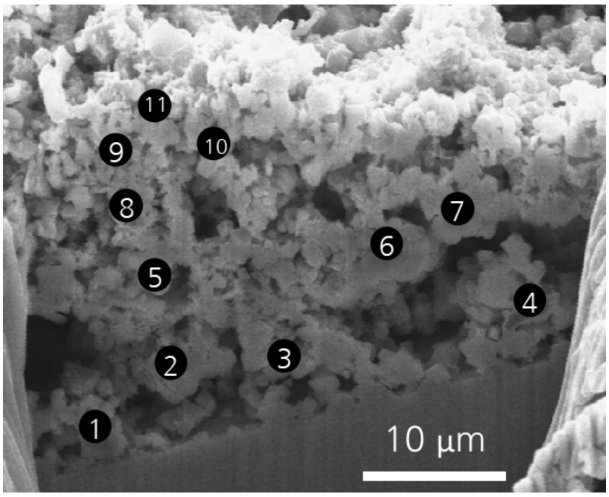

Fig. 4. Cross sectional SEM image of CRUD layer

Table I: Chemical composition of CRUD layer

#	O [at%]	Fe [at%]	Ni [at%]	Ni/Fe ratio
1	52.71	27.40	19.90	0.73
2	59.20	23.14	17.65	0.76
3	9.37	51.26	39.36	0.77
4	18.73	46.23	35.04	0.76
5	46.02	32.03	21.95	0.69
6	9.49	52.70	37.81	0.72
7	20.90	44.91	34.19	0.76
8	43.13	27.68	29.19	1.05
9	57.15	23.79	19.06	0.80
10	46.94	21.90	31.16	1.42
11	48.18	28.90	22.92	0.79

EDS cross-sectional analysis confirmed that the CRUD layer was primarily composed of O, Fe, and Ni, all of which were supplied from the coolant. The elemental distribution of Ni and Fe exhibited no significant variation from the CRUD/oxide interface to the outer CRUD/coolant interface, indicating a relatively uniform compositional profile across the thickness of the layer. In the vicinity of the CRUD/coolant interface, nanoscale granular nickel ferrite particles with sizes on the order of several tens of nanometers were predominantly observed, while acicular NiO particles, enriched in nickel content, were identified to a lesser extent. These findings suggest that CRUD formed under the KOH-pH6.9-DH25-168h condition maintains a stable Ni/Fe distribution through the thickness, with microstructural features characterized by fine granular nickel ferrite dominating the outermost surface.

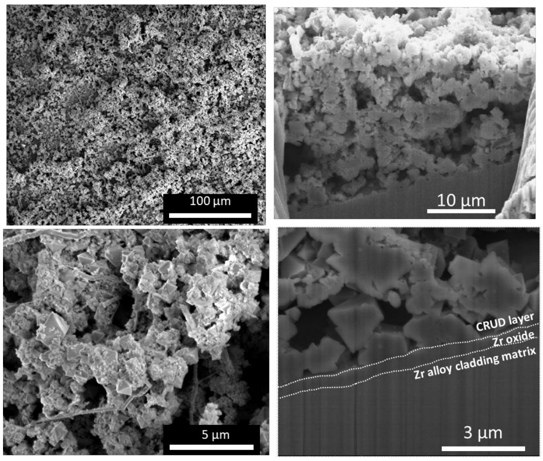

Fig. 5. Surface and cross sectional SEM images of CRUD layer

3. Conclusions

The deposited CRUD exhibited particle sizes predominantly in the range of 1–3 µm, while finer particles on the order of several tens of nanometers were also observed near the surface. The morphology of the CRUD was mainly granular, consisting of a mixture of polygonal $NiFe_2O_4$ particles and needle-shaped NiO particles. In addition, chimney-like porous structures were identified, extending through the CRUD layer and directly connecting to the cladding surface. The axial distribution of the Ni/Fe ratio showed no significant variation across the cross section. The average CRUD thickness was measured to be 22.48 µm, whereas the underlying zirconium oxide layer was confirmed to have a thickness of 0.62 µm. These findings collectively indicate that CRUD formed under the present experimental condition exhibits complex microstructural features and maintains a relatively uniform Ni/Fe compositional profile, while also contributing to a measurable but limited growth of the zirconium oxide film.

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