CRUD-Resistance Coating Effect on Fuel Cladding of a Pressurized Water Reactor

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TABLE II: Test matrix and experimental conditions

Experiment	Material	Time (days)	Ni [ppm]	Fe [ppm]	B [ppm]	Li [ppm]	T_{sur} [°C]	DO [ppb]	DH [cc/kg]
A	Zr alloy	7							
B	Zr alloy	14	24.82	17.75	1,200	2	346	< 10	25
C	TiN	7							
D	ZrN	14							

1. Introduction

As commercial nuclear power plants have been operated for a long time, some undesirable deposits have occurred on the upper side of the cladding surface [1]. This problem is caused by a combination of heat transfer and corrosion phenomena. When the cladding surface temperature increases above the coolant saturation temperature, sub-cooled boiling can occur at that point and form a porous corrosion-related unidentified deposits (CRUD).

CRUD can cause several problems during the normal operational period such as an axial offset anomaly (AOA) and a CRUD-induced localized corrosion (CILC). To mitigate these problems, a CRUD resistance coating on fuel cladding was applied using materials known to reduce the Van der Waals force between CRUD particles and the cladding surface and compared to commercial zirconium alloy cladding [2]. In this study, TiN- and ZrN-coating materials were selected as CRUD resistance coatings.

2. Experimental

2.1 Water Chemistry Condition

CRUD adhesion experiments were conducted under a typical water chemistry condition inside a PWR primary circuit; TABLE I.

TABLE I: Experimental conditions

	PWR	Test Condition
Pressure [MPa]	15.5	15.5
$T_{coolant}$ [°C]	320	323.5
Boron [ppm]	1,200	1,200
Lithium [ppm]	2	2
DH [cc/kg]	25	25
DO [ppb]	< 10	< 10
pH	6.8–7.4	6.8–7.4

To generate sub-cooled boiling, the target surface temperature was set as 346°C.

2.2 CRUD-Resistance Coating

To mitigate CRUD adhesion on the tube surface, two different coating materials were adopted which reduce Van der Waals force with CRUD particles compared to that of a zirconium alloy tube. Each material was coated using the physical vapor deposition (PVD) method in a vacuum state.

2.3 Test Matrix and Analysis

The experimental conditions were set to be identical. The test matrix for this study is summarized in TABLE II. CRUD distribution and cross-section figures were captured using focused ion beam – scanning electron microscopy (FIB-SEM) and chemical composition was measured using energy-dispersive X-ray spectroscopy (EDS).

3. Result

3.1 Experiment A

3.1.1 Surface

CRUD was randomly deposited on the heated surface but did not fully cover the whole surface because of the insufficient exposure time; Fig. 1. The average CRUD diameter was approximately 10 μm.
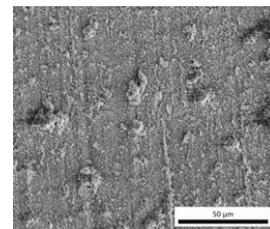
Fig. 1. Surface observation from experiment A

3.1.2. Cross Section

The thickness of the porous CRUD was measured at twenty different points and averaged; Fig. 2. The maximum thickness was approximately 9.28 μm and the minimum thickness was 4.60 μm. The average was 6.42 μm with a standard deviation σ= 1.56. The size of the CRUD particle near the heated surface is relatively larger than that of the outer CRUD layer.
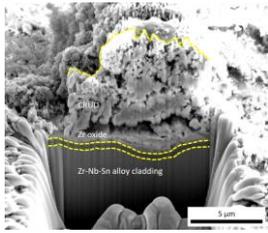
Fig. 2. Cross-section observation from experiment A

3.1.3. Chemical Composition

Chemical composition analysis was performed at four different points, such as the interface between the tube and CRUD. The information of the analyzed position and chemical composition for CRUD on the zirconium alloy tube are shown in Fig. 3 and TABLE III.
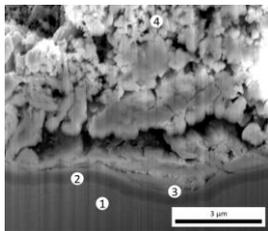
Fig. 3. EDS-analyzed points from experiment A

TABLE III: CRUD chemical composition from experiment A [at.%]

	O	Fe	Ni	Zr
1	11.73	1.05	1.28	85.94
2	37.06	1.36	5.98	55.60
3	54.90	4.67	40.43	-
4	48.83	18.63	32.54	-

It can be noted that point 1 consists of the zirconium alloy tube and point 2 is the zirconium oxide layer. Above the zirconium oxide layer there is a dense nickel oxide layer that formed on the spot where the sub-cooled boiling occurred [2]. At point 4 nickel and iron oxide combinations, such as nickel ferrite and nickel oxide, were deposited as CRUD.

3.2. Experiment B

3.2.1. Surface

CRUD was fully deposited on the surface but its size was too large to capture under the same magnification as that of experiment A; Fig. 4. Therefore, it was necessary to scale downward. The CRUD diameter varied from 30 to 180 μm.
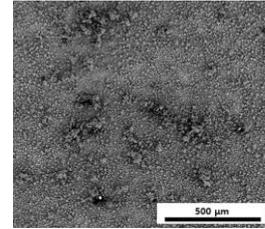
Fig. 4. Surface observation from experiment B

3.2.2. Cross Section

The CRUD chunk that had a diameter of approximately 180 μm was selected for cross-sectional observation as shown in Fig. 5. The maximum CRUD thickness from experiment B was approximately 91.08 μm and the minimum thickness was 82.45 μm. The average was 86.37 μm with a standard deviation σ= 2.10. The porosity and CRUD particle size increased.
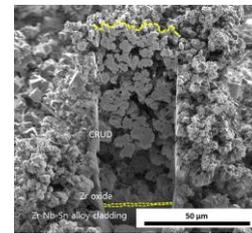
Fig. 5. Cross-section observation from experiment B

3.2.3. Chemical Composition

Chemical composition analysis was performed at five different points. EDS-analyzed points for the zirconium alloy tube are shown in Fig. 6 and the results listed in TABLE IV.
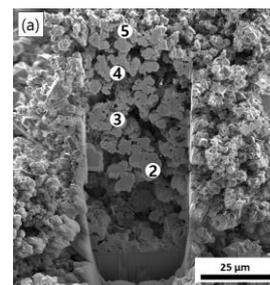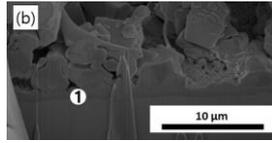
Fig. 6. EDS analyzed points of the (a) CRUD bulk and (b) nearby oxide layer from experiment B

TABLE IV: CRUD chemical composition from experiment B [at.%]

.	O	Fe	Ni	Zr
1	42.00	5.78	5.44	46.79
2	53.17	19.86	11.65	15.32
3	48.19	23.97	13.65	14.19
4	52.24	32.87	13.37	1.53
5	44.76	36.07	17.85	1.33

Compared to experiment A, the ratio of iron content increased up to approximately 40 at %. Thus, during the early CRUD depositional stage, CRUD mainly consists of nickel oxide but then changes to $Ni_xFe_{2-x}O_4$ where x can vary.

3.3. Experiment C

3.3.1. Surface

Compared to that of experiment A, the CRUD did adhere not only in terms of distribution but also by size of CRUD chunk, Fig 7.. The CRUD chunk diameter was from approximately 5 to 7 μm.
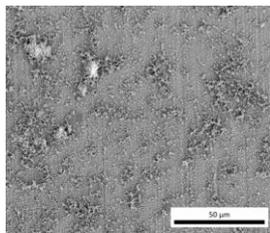
Fig. 7. Surface observation from experiment C

3.3.2. Cross Section

The major difference between experiments A and C is the existence of the zirconium oxide layer that formed immediately above the tube surface. In the case of the TiN-coated tube, the maximum CRUD thickness was 5.89 μm and the minimum was 2.80 μm. The average was 4.24 μm with a standard deviation σ=0.84.
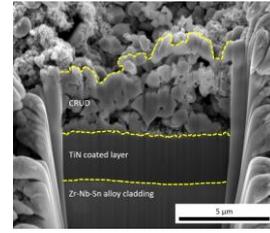
Fig. 8. Cross-section observation from experiment C

3.3.3. Chemical Composition

After a 7-day experimental period with the TiN-coated tube, there was no zirconium oxide layer and dense nickel oxide layer on the heated surface unlike the result of experiment A. CRUD was deposited on the TiN-coating layer with noticeable difference among points 1, 2, and 3. However, the iron ion composition ratio in CRUD was smaller than that of the zirconium alloy tube case. It seems that CRUD mainly consists of nickel oxide or nickel metal when the tube surface is coated with a TiN material; Fig. 9, TABLE V.
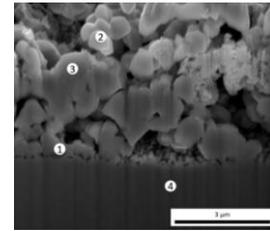
Fig. 9. EDS-analyzed points from experiment C

TABLE V: CRUD chemical composition from experiment C [at.%]

	N	O	Fe	Ni	Ti
1	-	66.65	9.10	24.25	-
2	-	63.71	6.83	29.45	-
3	-	64.82	5.54	29.63	-
4	11.09	9.30	0.47	0.67	78.46

3.4. Experiment D

3.4.1. Surface

A surface SEM image was taken where some peelings occurred to compare the CRUD chunk size on the surface and the peeling. If the CRUD chunk size on the surface is larger than that on the peeling, it can be expected that delamination might not have occurred or if it did it might have occurred during an early stage; thus, delamination has little effect on CRUD growth. CRUD was totally deposited on the surface, but a noticeable chunk did not occur. A surface SEM image is shown in Fig. 10.
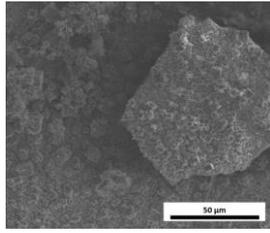
Fig. 10. Surface observation from experiment D

3.4.2. Cross Section

CRUD thickness was measured from the second ZrN coating layer to the CRUD deposited up to the peeling. The maximum CRUD thickness was 14.81 μm and the minimum was 2.99 μm. The average was 7.45 μm with a standard deviation σ=4.11; Fig. 11.
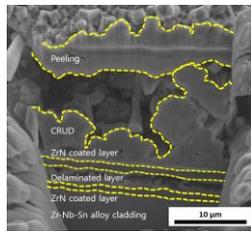
Fig. 11. Cross-section observation from experiment D

3.4.3. Chemical Composition
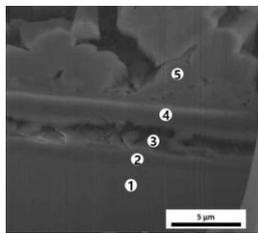
Fig. 12. EDS-analyzed points from experiment D

TABLE VI: CRUD chemical composition from experiment D [at.%]

	N	O	Fe	Ni	Zr
1	-	20.64	0.76	0.47	78.12
2	1.74	39.82	0.25	0.49	57.70
3	3.23	53.50	12.19	6.59	24.50
4	5.22	38.30	0.24	0.36	54.57
5	1.72	49.66	15.12	7.92	24.50

According to EDS measurement, Fig. 12 shows point 1 in a zirconium alloy tube cross section. Points 2 and 4 seem to be a ZrN-coating layer, but the zirconium element is overlapped with the base metal and the nitrogen element is difficult to distinguish using EDS. Considering the thickness of the coating layer is approximately 1 μm, from point 4 to 5 the parts

were detached from the ZrN-coating tube number 2, as shown in Fig. 10, during the early stage of the experiment and CRUD had deposited on it later on during the experiment. The composition of point 5 consists of nickel and iron but the amount is lower than that of the zirconium alloy tube. This result may have been caused by CRUD growth with the duration difference between the two cases.

4. Conclusion

The CRUD distribution and area fraction on the zirconium alloy tube was higher than that on the TiN-coated tube. The average CRUD thickness on the zirconium alloy tube was 6.42 μm with a standard deviation σ= 1.56 and that of the TiN-coated tube was 4.24 μm with a standard deviation σ= 0.84. The CRUD chemical composition on the zirconium alloy tube had a higher ratio of iron ion than that of the TiN-coated tube. The major difference between them was the existence of a zirconium oxide layer and dense nickel oxide layer at the innermost side of the heated surface.

Similar to the TiN-coated tube, the CRUD distribution and area fraction on the zirconium alloy tube was higher than that on the ZrN-coated tube. The average CRUD thickness on the zirconium alloy tube was 86.37 μm with a standard deviation σ= 2.10 and that of the ZrN-coated tube was 7.45 μm with a standard deviation σ= 4.11. The CRUD chemical composition on the zirconium alloy tube had a high ratio of iron ion that increased up to 36 at% when measured at a point far from the heated surface. This tendency may explain the formation of bonaccordite, which is a main cause of CIPS. In the case of the ZrN-coated tube, CRUD chemical composition showed a low ratio of iron and nickel ion compared to that of the zirconium alloy tube. Thus, CRUD could not sufficiently grow to become nickel ferrite.

The CRUD deposition phenomenon may be affected by several principles, such as the Van der Waals force [2], surface wettability [3, 4], and ion affinity [5]. Surface wettability can change microlayer properties that directly concern the bubble mechanism. Ion affinity can differ among the metal sources in the gap between the bubble and heated surface leading to a varied CRUD composition and can also slow or accelerate the CRUD depositional rate.

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