Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 7-8, 2015

The Oxidation Behaviors of Zry-4 and ZIRLO Tube Covered by CRUD in Steam and in Air

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1. INTRODUCTION

CRUD refers to deposit accumulated in the upper surface of a fuel rod. It forms as the corrosion products created in a primary system are moved to the surface of the nuclear fuel cladding as a result of coolant circulation. The high temperature of the core of a nuclear reactor accelerates the process by which CRUD absorbs boron as the surroundings of the nuclear fuel cladding develop into a subcooled nucleate boiling condition. The absorbed boron decreases neutron flux to incur an axial offset anomaly (AOA) [1]. Moreover, CRUD increases the amount of radiation dose in the primary system. Co and Ni are accumulated in nuclear fuel cladding to generate the phenomenon of activation, which eventually increases the radiation dose. To date, there is no domestic or international research data on the impact of CRUD on the nuclear fuel cladding surface. Hence, we examined the changes in oxidation behavior after the formation of CRUD in the interior of the nuclear fuel cladding.

2. EXPERIMENT

In this study, an oxidation test was performed at 700℃ ~ 1000℃ after creating simulated CRUD in the interior of a Zry-4 and ZIRLO tube in air and steam atmosphere.

2.1 Method

The specimen used in the test was a Zry-4 and ZIRLO tube. The composition of the specimen is summarized in Table 1.

Table 1. Composition of Zr alloy

	Zr	Nb	Sn	Fe	Cr
Zircaloy-4	Bal	-	1.35	0.2	0.1
ZIRLO	Bal	1.0	1.0	0.1	-

In order to form simulated CRUD in the specimen interior, an experimental device that can simulate the subcooled nucleate boiling phenomenon that occurs in the upper surface of a fuel rod was fabricated, as shown in Figure 1. The Zry-4 and ZIRLO specimen was connected to a pipe No. 3 to form CRUD in the tube interior. The temperature and pressure of the external heater were maintained at 350℃ and 150 bar, respectively. In order to form simulated CRUD at a rapid flow rate of approximately 3ml/min in five days, the concentration of the chemical composition of the metal ion was set at three times that of the actual coolant.

Table 2. Chemical composition of primary coolant in nuclear power plant [2]

	B	Li	Fe	Cr	Ni	Co
ppm	1000	3	25.68	2.37	1.35	0.24

Simulated CRUD was formed inside the Zry-4 and ZIRLO specimen and the specimen was cut into sections such that each had an external diameter of 7.8mm, a thickness of 0.75, and a height of 15mm.

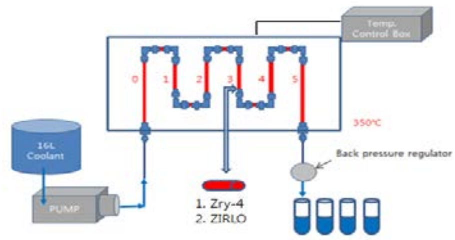

Figure 1. Mimetic diagram of CRUD-forming experimental device.

In order to observe the high-temperature oxidation behavior of each specimen covered with CRUD in air and steam atmosphere in transient conditions, the specimen was oxidized for 1000 ~ 5000 seconds at 700 ~ 1000℃ temperature, using a corrosion test device as shown in Figure 2. The change in weight of each specimen was subsequently measured.

Figure 2. High-temperature discontinuous measurement oxidation device (tube furnance).

3. RESULTS AND DISCUSSION

The interior of the specimen with simulated CRUD was checked by SEM analysis, as shown in Figure 3. While CRUD did not appear inside the regular Zry-4 and ZIRLO tube, grain-type CRUD appeared inside the Zry-4 and ZIRLO tube that had simulated CRUD.

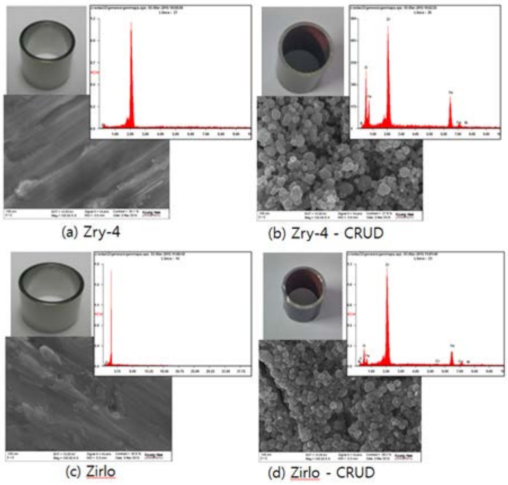

Figure 3. SEM image of no-CRUD and CRUD in Zr alloy interior.

An oxidation reaction test was conducted on CRUD and no-CRUD Zr alloy specimens using a tube furnance in air and steam atmosphere. Changes in the microstructure of the Zry-4 and ZIRLO cladding exterior were observed. A black protective oxidized layer appeared in general on the exterior of the Zry-4 cladding. As temperature/time increased, the color of the cladding exterior changed to light brown. Meanwhile, the ZIRLO cladding exterior lost its black protective oxidized layer surface to become white, differing from the Zry-4 specimen.

Figure 4. Image of 700~1000 ℃ oxidation specimen exterior in steam and air atmosphere.

Figure 5 shows the oxidation behavior of the Zr alloy by its weight change. As temperature/time increased, the change in weight of the Zry-4 and ZIRLO tube cladding also increased. This is because ZrO_2 and $2H_2$ are created when the Zr alloy shows an oxidation reaction on a metal surface, which generates heat that further accelerates oxidation [3]. The oxidation acceleration was more prominent in the steam atmosphere than in the air atmosphere. The oxidation process proceeded especially quickly in the case of oxidation at 900 ℃ ~ 1000 ℃, as the oxidized layer formation was accelerated.

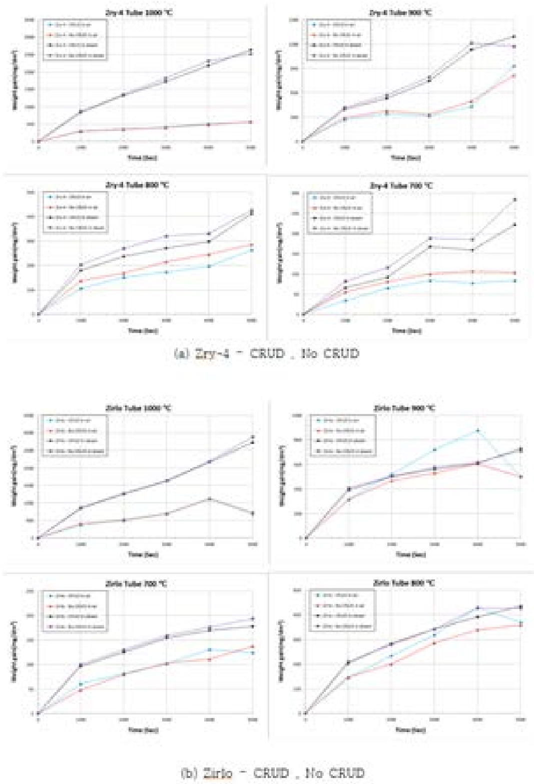

Figure 5. Comparison of weight change of Zry-4 and ZIRLO.

CRUD and no-CRUD formed in the Zr alloy tube interior were compared using optical microscopy. At 700 ~ 1000 ℃, the process of formation of the $\boldsymbol{\alpha}$-Zr and $\boldsymbol{\alpha}+\boldsymbol{\beta}$-Zr phase as temperature/time increased was similar in all cases. Figures 6 and 7 show the microstructure in conditions lower than 1000 ℃, which is similar to the microstructure image of the oxidized layer at 800 ~ 1000 ℃, as demonstrated by Nagase [4]. Although the oxidized layer formed at 700 ~ 800 ℃ existed in a smooth shape, an oxidized layer structure of columnar grains appeared in conditions of 900 ℃ ~ 1000℃. The thickness of the oxidized layer of CRUD and no-CRUD formed in the Zr alloy tube interior increased as temperature/time increased. However, the interior with CRUD showed a slight decrease in the thickness of the oxidized layer compared to the no-CRUD interior. This can be interpreted to mean that

CRUD formed in the Zr alloy interior played the role of a protective film preventing oxidation.

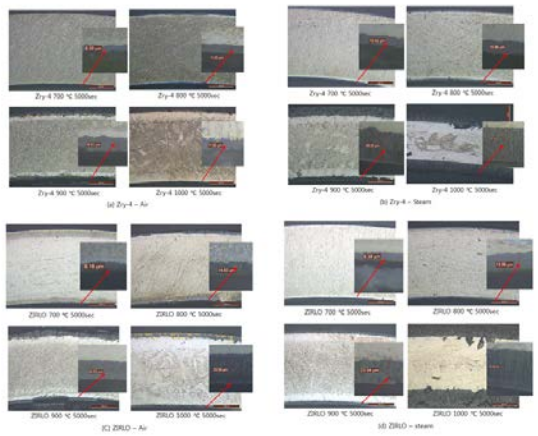

Figure 6. OM image of microstructure of CRUD layer in Zr alloy interior by each temperature.

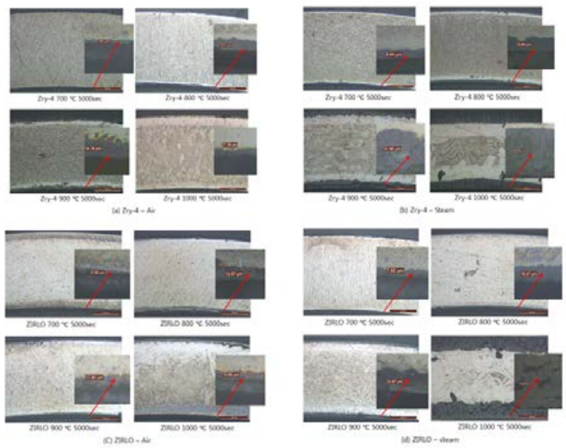

Figure 7. OM image of microstructure of no-CRUD layer in Zr alloy interior by each temperature

4. CONCLUSIONS

In this study, an oxidation test was performed at 700 ℃ ~ 1000 ℃ in steam and air atmosphere by forming CRUD in the interior of Zry-4 and ZIRLO. CRUD and no-CRUD layers were compared in the Zr alloy interior and the change in the amount of oxidation was measured according to the temperature and time. In the test, a black protective oxidized layer appeared on the Zry-4 and ZIRLO exterior. As the temperature or time increased, this layer changed to light brown or while, losing its protective properties. Moreover, CRUD created in the Zr alloy interior showed a slight decrease of the thickness in its oxidized layer compared to the case of no-CRUD. It is conjectured that the CRUD layer prevents oxidation by forming a protective film.

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