Evaluation of a Breakaway Oxidation of Zr-based Claddings after a LOCA-simulated Oxidation and Water Quenching Test

Hyun-Gil Kim*, Il-Hyun Kim, Byung-Kwan Choi, Jeong-Yong Park, Yong-Hwan Jeong
Advanced Core Materials Lab, KAERI, Daedeokdaero 1045,Yuseong, Daejeon 305-353, South Korea
**Corresponding author: hgkim@kaeri.re.kr*

1. Introduction

Zirconium alloys have been used as a fuel cladding material for several decades, since these alloys have revealed a good corrosion resistance and mechanical properties in reactor operating conditions. At present, the corrosion of fuel cladding is the most critical problems for high burn-up operating target of LWRs. And it is of importance that the fuel cladding should maintain their nature at a postulated design-based accident such as LOCA (loss of coolant accident).

LOCA is treated as one of the most important design-basis accidents. The fuel cladding is faced to the high temperature oxidation and then quenched by water following the ECCS (emergency core cooling system) progress during the LOCA event [1]. So, the Zr-based fuel cladding loses their integrity by the formation of the ZrO_2 phase and oxygen stabilized α-Zr layer [2]. Since the brittle behavior of cladding materials was increased by increasing the fraction of the ZrO_2 phase and oxygen stabilized α-Zr layer, the ductility of the Zr-based fuel cladding is decreased after LOCA event. During the LOCA-simulated oxidation test, the breakaway phenomenon of oxidation rate was reported [3], and this breakaway phenomenon was considerably shown at the test temperature about 1000 ℃ as well as at the long term test periods more than 2000 s.

Although the breakaway oxidation phenomenon was considerably treated in the LOCA event, the study on the break oxidation behavior of the Zr-based cladding during the LOCA-simulated test is insufficient. So, the object in this work is to evaluate the breakaway oxidation behavior of the Zr-based claddings after LOCA-simulated oxidation and water quenching test.

2. Methods and Results

Four types of Zr-based claddings, as shown in Table 1, in a length of 200 mm were oxidized at the temperature of 1000 ℃ and exposed at different times of 300 s, 2000 s, 3000 s, and 5000 s. And it was cooled at the intermediate temperature of 700 ℃ for 100 s after being oxidized in steam environment and then quenched by water. Fig. 1 shows an illustration of LOCA test scheme.

The ring compression test and the microhardness test were carried out to evaluate the ductility for the simulated LOCA tested claddings. The optical microscope observation was performed to calculate the fraction of the ZrO_2 phase and the oxygen stabilized α-Zr layer and to observe the shape of the oxygen stabilized α-Zr layer and prior-β phase with the test conditions and alloy composition of claddings.

Table 1 Chemical composition of Zr-based cladding materials in weight percent

ID	Nb	Sn	Fe	Cr	Cu	Zr
HANA-5	0.4	0.8	0.35	0.15	0.1	Bal.
HANA-6	1.1	-	-	-	0.05	Bal.
Alloy-A	1.0	1.0	0.1	-	-	Bal.
Zircaloy-4	-	1.5	0.2	0.1	-	Bal.

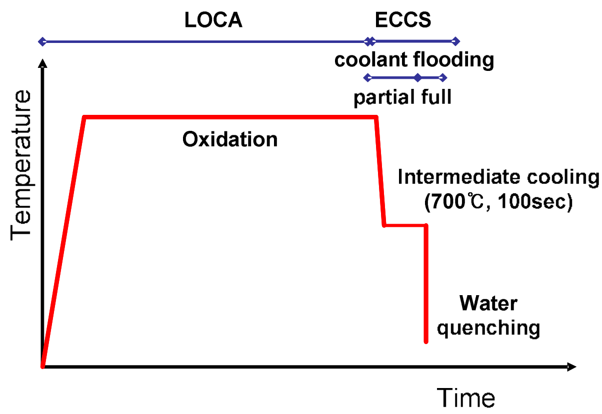

Fig. 1 Illustration of the LOCA-simulated oxidation and water quenching test scheme

Fig. 2 shows the surface appearances of the cladding tubes in the middle area after the LOCA-simulated test. The black oxide was observed at all cladding materials after the exposure time of 300 s and 2000 s at the temperature of 1000 ℃. However, the surface appearance was changed with the cladding materials after an exposure time of more than 2000 s. In the HANA-5 and HANA-6 claddings, the black oxide was maintained up to 5000 s in exposure time, whereas the black oxide was changed to a white oxide in the Alloy-A and Zircaloy-4 claddings. Especially, the white spot was shown in the Alloy-A after the 3000 s test.

The surface color during the oxidation test was influenced by the chemical stoichiometry of oxide layer. This is that the change of color from black to white was caused by non-stoichiometric characteristics such as ZrO_{2-n}. This color change in the Zr-based alloys was shown in the case of corrosion rate acceleration such as breakaway oxidation [4]. So, it could be recognized that the HANA-5 and HANA-6 claddings showed a higher resistance for the breakaway oxidation behavior than the Alloy-A and Zircaloy-4, since the breakaway oxidation behavior occurred in the Alloy-A and Zircaloy-4 claddings.

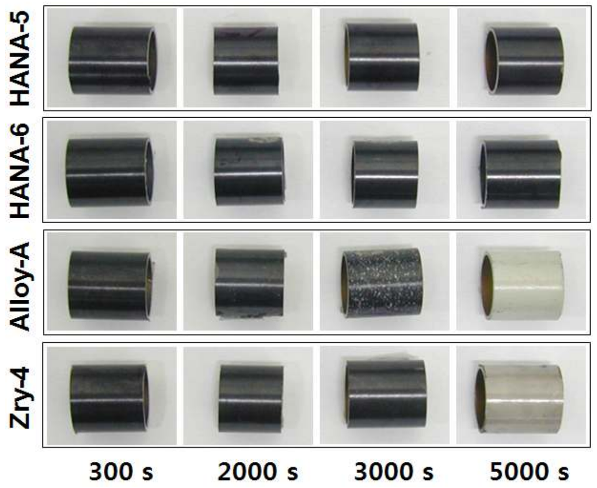

Fig. 2 Surface appearances of the cladding tubes in the middle area after the LOCA-simulated test

From the ring compression test after oxidized and quenched claddings in the oxidation time ranged from 300 s to 5000 s at 1000 ℃ as shown in Fig. 3, the load drop in the stress-strain curve was not observed in the three tested claddings except for Zircaloy-4 cladding after the 300 s oxidation, whereas, the load drop was observed in all tested claddings after the oxidation time more than 2000 s. The value in both maximum load and displacement was taken at the highest position in the stress-strain curve at the first road drop.

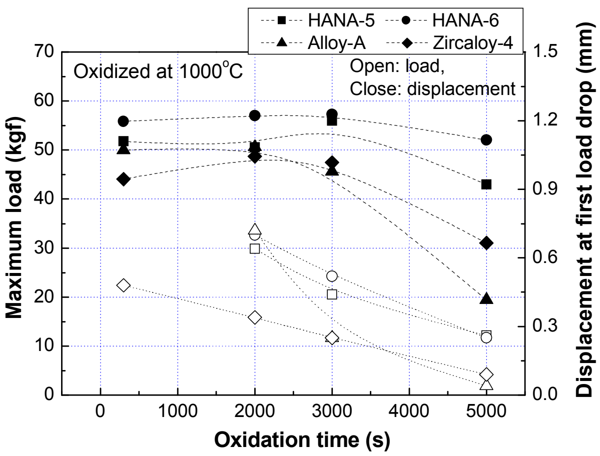

Fig. 3 Pole figure results of the HANA-4 alloy sheets for the normal direction

The maximum load was considerably decreased in the Alloy-A and Zircaloy-4 claddings after the oxidation time of 5000 s when compared to the HANA-5 and HANA-6 claddings. The value of displacement at the first load drop was decreased with increasing the oxidation time in all cladding materials. However, that of displacement was very low in the Alloy-A and Zircaloy-4 claddings when compared to the HANA-5 and HANA-6 claddings. Since the low displacement value was caused by the brittle characteristics of oxidized Zr-based materials, the ductility of HANA-5 and HANA-6 claddings was higher than the Alloy-A and Zircaloy-4 claddings. It is assumed that the low ductility value of the Alloy-A and Zircaloy-4 was related to the breakaway oxidation behavior at 1000 ℃.

From the observation of the ZrO_2 phase and the oxygen stabilized α-Zr layer by using the optical microscope, the load drop and the decrease of the ductility were matched with increasing the oxygen stabilized α-Zr layer thickness. And the ZrO_2 phase thickness was considerably increased in the Alloy-A and Zircaloy-4 claddings after the breakaway oxidation. So, it is assumed that the breakaway phenomenon during a high temperature oxidation should be related to the chemical composition of Zr-based cladding materials.

3. Conclusions

To evaluate the breakaway oxidation behavior of Zr-based cladding materials, the LOCA-simulated test was conducted at 1000 ℃ up to 5000 s.

The HANA-4 and HANA-6 cladding materials showed a higher resistance for the breakaway oxidation behavior than the Alloy-A and Zircaloy-4.

The breakaway phenomenon during a high temperature oxidation at 1000℃ was related to the composition of the cladding materials.

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