Analysis of Breakaway Oxidation Behavior of Zr Claddings after LOCA Simulation Test

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1. Introduction

It is of importance that the fuel cladding should maintain their nature at a postulated design-based accident such as loss of coolant accident (LOCA). During the LOCA event, the fuel cladding is faced to the ballooning, high temperature oxidation, and quenched by cold water due to the emergency core cooling systems (ECCS) [1]. The fuel cladding loses their integrity by the formation of oxide (ZrO_2) and oxygen stabilized α-phase (α-Zr(O)), since ZrO_2 and α-Zr(O) phases had a brittle property in cladding materials [1,2]. As well as the cladding ductility decreased as the oxygen concentration in the prior-β phase increased [2].

Sometimes, a breakaway oxidation phenomenon was happened during the high temperature oxidation test [3,4]. Regarding the breakaway oxidation, the cladding integrity is considerably decreased after the breakaway oxidation because of the steep increase of oxide thickness and hydrogen pickup after breakaway oxidation. An oxide crystal structure was considered as an important factor to analyze the breakaway oxidation kinetics of zirconium claddings because the phase transformation between tetragonal and monoclinic oxide imposed on the formation of cracks and pores in the oxide layer [3, 4]. The objective of this work is to analysis the breakaway oxidation behavior of zirconium fuel cladding during the LOCA simulation test. For this purpose, cladding materials were exposed at the high temperature steam environment at 1000 °C up to 5000 s to obtain the breakaway phenomenon. And the micro-structural observation and the crystal structure analysis for the claddings of before and after breakaway were done to find out the breakaway mechanism during the LOCA event.

2. Methods and Results

Table 1 shows the chemical composition of HANA (HANA-5 and HANA-6), Alloy-A and Zircaloy-4 claddings. The outer diameter is 9.5 mm and wall thickness is 0.57 mm in all tested claddings.

Table.1: Chemical composition of zirconium fuel claddings for LOCA-simulation test

Alloy	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.

To simulate a LOCA, the claddings with a length of 200 mm were oxidized by steam at the temperature of 1000 °C from 300 s to 5000 s. After being oxidized in a steam environment, the oxidized claddings were cooled to the intermediate temperature of 700°C and maintained for 100 s and then quenched by water. All claddings were oxidized on the single outer surface. A direct heating by the ohmic resistance was applied to heat the cladding specimens. The temperature of specimens was measured by using a pyrometer, which was connected to a computer to control the specimen heating.

The observation of microstructure was performed by using optical microscope (OM) and scanning electron microscope (SEM) equipped with energy dispersive spectra (EDS) to analyze the characteristics of ZrO_2 phase, α-Zr(O) layer, and prior-β region after the LOCA-simulation test.

Hydrogen uptake in the oxidized cladding was measured by a vacuum fusion method (LECO, Model RH-404). The hydrogen analysis was performed using the piece of 2-3 mm sectioned from the ring compression tested samples.

The oxide phase formed on the cladding surface was analyzed by using the high temperature X-ray diffractometer (Rigaku, Model D/MAX 2500H). The samples were tested at the room temperature, 1000, 1250°C and the heating rate was 20°C/min in a vacuum condition.

2.1 Surface appearance

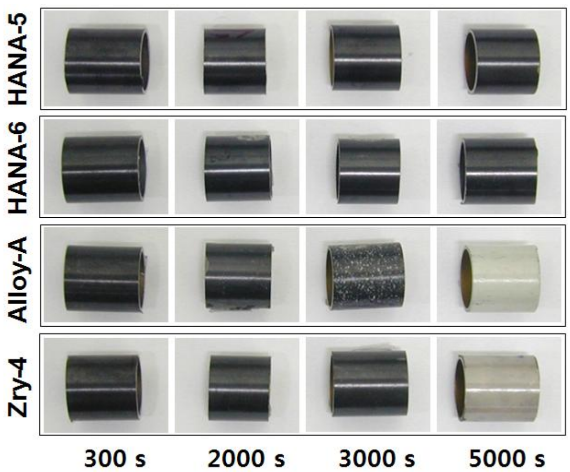

Fig. 1. Surface appearance of the LOCA-simulation tested cladding materials at 1000 °C as a function of test time.

Fig. 1 is the surface appearance of the LOCA simulation tested claddings. From this, it is known that the breakaway phenomenon, which could be identified by a cladding surface color of white, was shown at Alloy-A and Zircaloy-4 claddings, however, that phenomenon was not observed at two HANA claddings after a 5000 s test. So the breakaway resistance of two HANA claddings is higher than that of Alloy-A and Zircaloy-4 claddings. This result is well matched with the previous study performed by using the thermo-gravimetric analyzer (TGA) at 1000 ℃ [4].

2.2 Micro-structural analysis

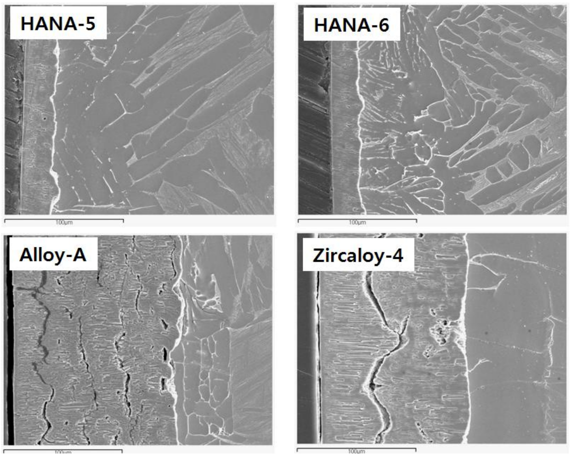

Fig. 2. Cross-sectional SEM observation of the LOCA-simulation tested cladding materials at 1000 ℃ for 5000 s.

Fig. 2 shows the cross-sectional observation of the oxidized claddings exposed at 1000 ℃ for 5000 s. The oxide layer thickness is considerably increased in the Alloy-A and Zircaloy-4 claddings when compared to the HANA-5 and HANA-6 claddings, because the breakaway oxidation occurred in Alloy-A and Zircaloy-4 claddings at the test time before 5000 s. The measured oxide thickness of both HANA-5 and HANA-6 claddings is lower than 35 μm, but that of both Alloy-A and Zircaloy-4 claddings is higher than 100 μm. And it is shown that the oxide layer is divided into 4 in Alloy-A and 2 in Zircaloy-4. So, the layered oxide was formed by breakaway during the LOCA simulation test.

2.3 Hydrogen analysis

Form the hydrogen analysis with the oxidation time, the hydrogen content of HANA-5 and HANA-6 claddings maintained about 50 ppm up to 5000 s test, however, that content of Alloy-A and Zircaloy-4 increased more than 100 ppm before breakaway oxidation. Therefore, the breakaway oxidation was related to the hydrogen uptake during the high temperature oxidation.

2.4 Oxide crystallographic analysis

The tetragonal and monoclinic phase peaks were observed from the oxide analysis. The relative intensity of tetragonal phase was lower than 5% tested at room temperature and 1000℃ from 300 s to 5000 s for all claddings. So, the breakaway oxidation kinetics during the LOCA could not be explained by the oxide phase transformation behavior of Alloy-A and Zircaloy-4 claddings.

3. Conclusions

From the LOCA simulated high temperature oxidation test, HANA-5 and HANA-6 claddings showed better breakaway resistance than Alloy-A and Zircaloy-4 claddings. The breakaway oxidation was related to the hydrogen uptake during the high temperature oxidation. It was impossible to find out the correlation between oxide crystal structure and breakaway oxidation kinetics.

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