Consideration of Breakaway Oxidation Mechanism of Fuel Cladding tested at 1000°C

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1. Introduction

A breakaway oxidation phenomenon could be happened during the high temperature oxidation [1, 2]. 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. However, the mechanism of breakaway behavior was not clearly defined at the present time. A phase transformation of 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 [1-3]. But the phase transformation temperature of oxide was not matched to the temperatures of breakaway oxidation occurrence in a short time at about 760℃ and 1000℃ [4]. So, the objective of this study is to analyze the breakaway oxidation mechanism of zirconium fuel claddings which were tested at the high temperature steam environment at 1000℃ up to 5000 s. And the microstructural observation and the crystal structure analysis for the claddings as well as oxides were performed to find out the breakaway mechanism at the high temperature oxidation.

2. Methods and Results

2.1Test and analysis methods

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

Cladding	Alloy Composition (in wt%)					
	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.

Table 1 shows the chemical compositions of the four types of cladding materials of HANA (HANA-5 and HANA-6), Alloy-A and Zircaloy-4. The outer diameter is 9.5 mm and wall thickness is 0.57 mm in dimensions of all tested claddings. The claddings with a length of 200 mm were exposed in a steam environment at the temperature of 1000℃ from 300 s to 5000 s. After being oxidized in a steam flow condition, 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 and scanning electron microscope equipped with energy dispersive spectra to analyze the cross-sectional characteristics of ZrO_2 phase, α-Zr(O) layer, and prior-β region after the steam environment corrosion 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.

2.2 Microstructural observation after the oxidation test

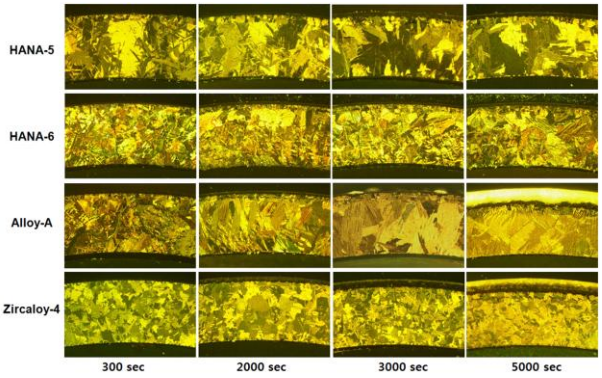

Fig. 1. Surface appearance of the LOCA-simulation tested cladding materials at 1000℃ as a function of test time.

Fig. 1 shows the cross-sectional observation of the cladding materials tested at a steam environment at 1000℃ up to 5000 s. From this microstructural appearance, it could be recognized that the breakaway phenomenon, which could be identified by a oxide color as a white and higher increase of oxide layer thickness after a 5000 s test, was shown in Alloy-A and Zircaloy-4 claddings, whereas, that phenomenon was not observed at two HANA claddings. From this result, the breakaway resistance of two types of HANA claddings is higher than those of Alloy-A and Zircaloy-4 claddings.

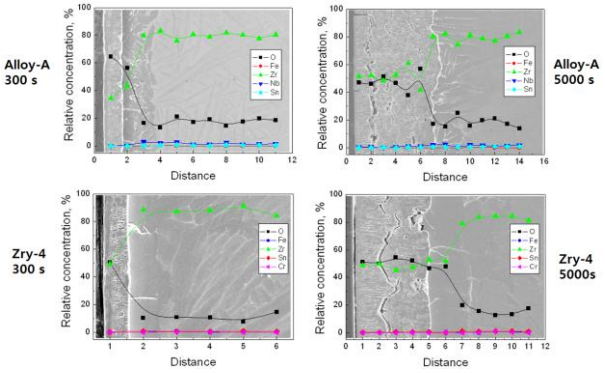

Fig. 2. Cross-sectional SEM observation of the cladding materials tested at 1000 ℃ for 300 s and 5000 s.

Fig. 2 shows the cross-sectional observation of the oxidized Alloy-A and Zircaloy-4 claddings exposed at 1000℃ for 300 s and 5000 s. This figure shows the difference of oxide layer characteristics before and after breakaway oxidation. The oxide layer thickness after 5000 s test in the Alloy-A and Zircaloy-4 claddings is considerably increased when compared that after 300 s test, and some lateral cracks are formed in the oxide layer of Alloy-A and Zircaloy-4 claddings after 5000 s test. The size of cracks formed in Zircaloy-4 oxide is more large and wavy than that of cracks formed in Alloy-A oxide. The oxide thickness of both HANA-5 and HANA-6 claddings is not considerably increased after 5000 s test. The lateral cracks in oxide were formed after breakaway oxidation.

2.3 Hydrogen content analysis

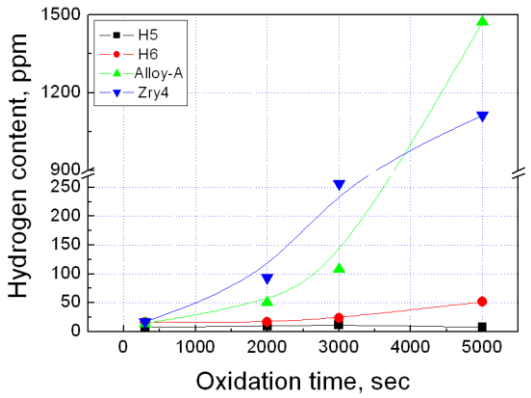

Fig. 3. Hydrogen content analysis of the cladding materials with the oxidation time tested at 1000℃.

From 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 hydrogen uptake was related to the breakaway oxidation phenomenon during the high temperature oxidation.

2.4 Oxide crystallographic analysis

The tetragonal and monoclinic phase peaks were analyzed by using the HT-XRD at the test temperature of RT, 1000℃, and 1250°C. The relative intensity of tetragonal phase was lower than 5% tested at RT and 1000℃ for all claddings, whereas, the intensity of tetragonal phase was reached to 100% tested at 1250℃. The oxide phase transformation behavior formed on the cladding materials by steam corrosion is following the ZrO_2 phase transformation temperature between monoclinic to tetragonal. So, the breakaway oxidation of Alloy-A and Zircaloy-4 at 1000℃ could not be explained by the oxide phase transformation behavior.

3. Conclusions

HANA-5 and HANA-6 claddings showed better breakaway resistance than Alloy-A and Zircaloy-4 claddings after a steam environment oxidation test at 1000°C. After the breakaway oxidation, the hydrogen uptake was considerably increased in Alloy-A and Zircaloy-4. It was impossible to find out the correlation between oxide crystal structure and breakaway oxidation kinetics at 1000°C steam oxidation test.

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