Effects of Pre-oxide and Pre-hydride on High-Temperature Oxidation of Advanced Fuel Claddings at LOCA Temperatures

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1. Introduction

During the LOCA condition, the fuel claddings are subjected to a high temperature oxidation which finally quenched because of the emergency coolant reflooding into the reactor core. In this condition, the equivalent cladding reacted (ECR) should not exceed the criterion of 17% and the peak cladding temperature (PCT) should also be below 1200°C [1]. It is very important to elucidate the high-temperature oxidation behaviors of advanced claddings, especially pre-oxided and pre-hydrided states, because of the difference of chemical composition between Zircaloy-4 and advanced claddings [2,3,4]. In this study, it was investigated that the effects of pre-oxide and pre-hydride on high-temperature oxidation behaviors of advanced claddings in LOCA temperature ranges.

2. Experimental

The test specimens for the pre-treatment (i.e. pre-oxide and pre-hydride) were cut off from two cladding tubes (Zircaloy-4 & A-Cladding). The size of the specimen was about 8 mm in length. The pre-oxidation was carried out in a static autoclave under the 450°C steam condition to achieve an equal-oxide thickness of 6~7 μm. And the pre-hydrided specimens were obtained by a use of gas charging method. The hydrogen contents in the hydrided specimens were analyzed from 300 to 350 ppm.

The apparatus for the high-temperature testing was established by modifying the Shimadzu TGA (Thermo-gravimetric Analyzer, TGA 51H). The heating rate up to the desired temperature was set at 50°C/min. After the oxidation testing at the temperatures of 900 to 1200°C for 40 minutes, the surface appearance and microstructures of all the tested specimens were observed by a polarized optical microscope.

3. Results and Discussion

3.1 Oxidation Behaviors

The weight gains of the pre-oxides specimens increased with an increase of oxidation temperatures according to the parabolic rate. The oxidation resistances of A-Cladding at all oxidation temperatures were superior to those of Zircaloy-4. This could be resulted from the difference of the chemical composition between two claddings. Nb was added in A-Cladding but not in Zircaloy-4. So, Nb could play a role in improve the oxidation resistance of A-Cladding at 900~1200°C. And the weight gain difference between two claddings at each temperature decreased with an increase of oxidation temperature. But, the temperature effects could be more dominant than the alloying effects at higher temperatures.

Compared with the as-received claddings, the weight gains of pre-hydrided cladding at same oxidation temperature were lower than that of the as-received cladding. The pre-oxided layer, which was formed at 450°C, could retard the oxygen diffusion through the pre-oxide layer during the oxidation at 900~1200°C since the oxide layer formed at 450°C were denser than that formed at 900~1200°C [5,6].

In the case of pre-hydrided claddings, the weight gains of the pre-hydrided claddings were the same trends of pre-oxided claddings as the oxidation temperature increased. But the weight gains of the hydrided claddings at same temperature were larger than those of the as-received claddings. The oxidation resistances of A-Cladding at all oxidation temperatures were also superior to those of Zircaloy-4. The hydride effects on the oxidation rate at LOCA temperature did not understand yet.

In shorts, the pre-oxide could improve the oxidation resistance at LOCA temperatures but the pre-hydride could deteriorate the resistance.

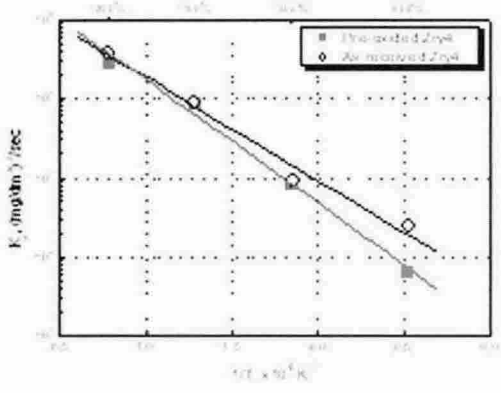

Fig. 1 Oxidation rate constants of Zircaloy-4

3.2 Surface Appearance

After the oxidation tests at 900~1200°C, the surface appearances were observed for all specimens. The colors of the pre-oxided specimens were changed from the dark black to gray as the oxidation temperature

increased. In the case of pre-oxided Zircaloy-4, the white spots were revealed on its outer surface at 1000°C. And the pre-oxide layer of A-Cladding was spalled out after the 1000°C oxidation. The complex phenomena at 1000°C could be related to the transformation of oxide structures from monoclinic ZrO_2 to tetragonal ZrO_2 [7]. It is necessary to study in depth to understand the relationship between oxidation behaviors between the oxide transformations.

The trends of the color change in pre-hydrided specimens were almost the same of pre-oxided ones. However, the spallation of surface layer was not detected at 1000°C. The color of pre-hydrided Zircaloy-4 was more grayish than that of A-Cladding at same oxidation temperature. This was well agreed with the change of weight gains, as previous mentioned.

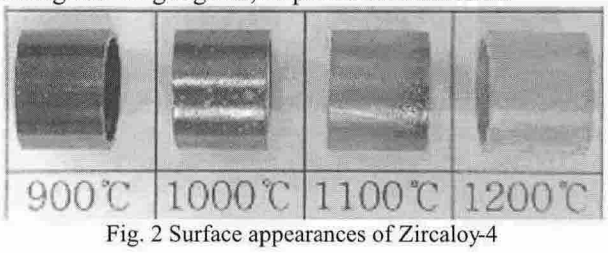

Fig. 2 Surface appearances of Zircaloy-4

3.3 Microstructures

The microstructures after the oxidation at 900°C showed the two phases including the α+β Zr for the pre-oxided and pre-hydrided specimens. But the grain of A-Cladding was smaller than that of Zircaloy-4 because of Nb addition in A-cladding. In the β phase region at above 1000°C, the O-stabilized α-Zr layer was clearly observed between the oxide layer and prior-β layer for the pre-oxided and pre-hydrided Zircaloy-4. But the O-stabilized α-Zr layer in A-Cladding could not be clearly clarified between the oxide and prior-β layers. The O-stabilized α-Zr phases could be in cooperated into prior-β phases for the A-Cladding. This could be interpreted from results of the Nb addition in A-Cladding [8,9].

The Sn segregation line in the Zircaloy-4 oxide layers were easily detected at 1200°C. But the line could not be detected in the oxide layers of A-Cladding. The disappearance of the Sn segregation line in the A-Cladding oxide layers cannot be explained yet. But the disappearance of the Sn line in the A-Cladding would be also related to the Nb addition.

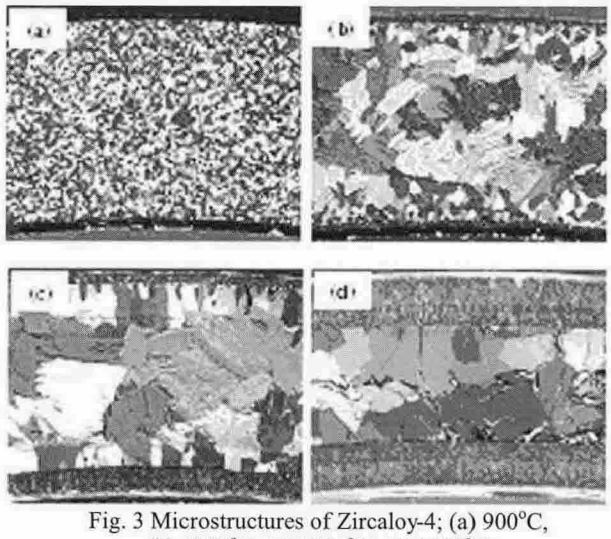

Fig. 3 Microstructures of Zircaloy-4; (a) 900°C, (b) 1000°C, (c) 1100°C, (d) 1200°C

4. Conclusions

1. The pre-oxide could improve the oxidation resistance at LOCA temperatures (900~1200°C) but the pre-hydride could deteriorate the resistance.
2. The colors of the pre-oxided or the pre-hydrided Zircaloy-4 and A-Cladding were changed from the dark black to gray as the oxidation temperature increased.
3. The O-stabilized α-Zr phases could be in cooperated into prior-β phases for the A-Cladding.
4. The Sn segregation line in the Zircaloy-4 oxide layers was easily detected at 1200°C but was not detected in the oxide layers of A-Cladding.

ACKNOWLEDGEMENT

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