

High-temperature Oxidation Behaviors of the Combined Pre-hydrided/Pre-oxidized HANA-4 Claddings at LOCA temperatures of 900 to 1200°C

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1. Introduction

Since 1997, KAERI has developed advanced cladding, which is named by HANA claddings, for the high burn-up nuclear fuel. The HANA claddings were being tested to verify their performances in the out-of-pile and the in-pile conditions. Until now, the test results in both conditions showed excellent when compared with a commercial reference cladding. High-temperature oxidation properties of HANA claddings were also characterized at the pre-oxidized and the pre-hydrided states as well as the as-fabricated state [1,2]. The pre-oxide could affect the oxidation kinetics at LOCA temperatures, while the pre-hydride could not influence the high-temperature oxidation kinetics [2]. In this study, it was investigated that the effects of the combined pre-oxide and pre-hydride, which could simulate a cladding state to be burned at the higher burn-up above 40,000 MWD/MTU, on the high-temperature oxidation behaviors at LOCA temperatures of 900 to 1200°C.

2. Experimental

The test claddings used in this study were HANA-4 and Zircaloy-4. Before the oxidation tests, the claddings were hydrided and then oxidized in order to simulate the burned cladding states of 40,000 and 60,000 MWD/MTU. The hydrides within the claddings were prepared by a use of gas charging method. Then the hydrogen charged claddings were sequentially oxidized under the 500°C air condition to form a thick oxide layer. The hydrogen contents and the oxide thickness of 40,000 MWD/MTU simulated claddings were about 250 ppm and 30 μm , respectively. And that contents and that thickness of 60,000 MWD/MTU were nearly 600 ppm and 80 μm , respectively.

The apparatus for the high-temperature testing was established by modifying the Shimadzu TGA (Thermogravimetric Analyzer, TGA 51H). The heating rate up to the desired temperature was set at 50°C/min. It was elucidated that the oxidation behaviors, surface appearance and microstructures after the oxidation testing at the temperatures of 900 to 1200°C for 2400 s.

3. Results and Discussion

3.1 Oxidation Behaviors

The weight gains of the combined HANA-4 claddings having 250 ppm H (hydrogen)/30 μm OT (oxide thickness) increased according to the parabolic oxidation rate when the oxidation time increased. The increase of the oxidation temperature accelerated the weight gains of the cladding. In the case of the HANA-4 cladding having 600 ppm H/80 μm OT, the oxidation kinetics was also controlled by the parabolic rate similar to those of the claddings having 250 ppm H and 30 μm in oxide thickness.

At a specific oxidation temperature, the weight gains of HANA-4 claddings decreased with the hydrogen contents and the oxide thickness. That is, the combined hydrides and oxides retarded the oxidation rate. It was interpreted that the oxygen diffusion could retard within the pre-oxide layer, which was denser than that formed at 900 to 1200°C. The oxide property could affect the oxidation kinetics.

The Zircaloy-4 claddings which were combined the hydrides and oxides showed the similar oxidation behaviors of HANA-4 claddings. The simultaneously combined Zircaloy-4 claddings were obeyed by the parabolic rate. The weight gains of the 250 ppm H/30 μm OT Zircaloy-4 claddings were lower than those of the fresh Zircaloy-4 claddings at a same oxidation temperature. This could be resulted from the denser pre-oxide effects. In the 600 ppm H/80 μm OT Zircaloy-4 claddings, however, the pre-oxides did not affect the retardation of the oxidation rate. The vertical cracks through the oxide layer of the 600 ppm H/80 μm OT Zircaloy-4 claddings were easily observed from the oxide before the oxidation test. It was thought that the vertical penetration cracks should accelerate the oxidation reaction, so the oxidation rates could enhance when compared with those of the 250 ppm H/30 μm OT Zircaloy-4 claddings.

As mentioned above, the kinetics of all tested claddings was controlled by the parabolic rate. The parabolic rate constant (K_p) could be calculated from the relationship between the weight gains and the oxidation time at an oxidation temperature. Figure 1 represents the parabolic

rate constant (K_p) of the HANA-4 claddings. The rate constant shows the linearity on the reciprocal oxidation temperatures. The rate constant of the claddings increased with an increase of the oxidation temperature. It means that the oxidation rate should be depended on the oxidation temperature. The rate constants of the hydrided/oxidized claddings were lower than those of the fresh claddings. The pre-formed hydride/oxide could reduce the oxidation rate.

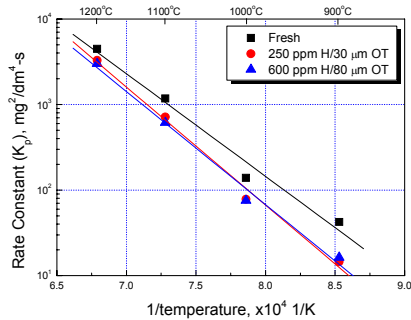


Fig. 1 Parabolic rate constants of HANA-4

3.2 Surface Appearance and Microstructures

After the oxidation tests at 900~1200°C for 2400 s, the surface appearances were observed for all samples. The color of the as-hydrided/oxidized (A/T) HANA-4 cladding was brown. As the oxidation temperature increased, the colors of the samples were changed from the brown to the white gray. When the hydrogen contents and the oxide thickness increased, the trends of the surface colors did not changed for the HANA-4 claddings (Fig. 2).

In the case of the Zircaloy-4 claddings, the surface colors were changed from the brown to the gray with an increase of the oxidation temperature. But the oxidized samples at the LOCA temperatures showed occasionally the surface cracks dissimilar to the HANA-4 claddings. The surface cracks were easily observed in the Zircaloy-4 claddings having higher hydrogen contents and thicker oxide thickness.

The oxide layer was newly formed between the pre-oxide and the metal matrix when the simulated claddings were oxidized at 900 to 1200°C under the steam atmosphere. The newly formed oxide thickness of the HANA-4 claddings increased with an increase of oxidation temperature. The newly formed oxides at 1200°C showed clearly the columnar structures. And a few vertical cracks were revealed in the HANA-4 previous oxide layer but the cracks did not penetrate the whole previous oxide thickness. They were existed at the outer part of the oxide layer.

The oxide growth trends of the Zircaloy-4 claddings were similar with the HANA-4 claddings. But the newly formed oxides of the Zircaloy-4 claddings were thicker than those of the HANA-4 claddings at the same

oxidation temperature. Some vertical was occasionally observed for the higher hydrogen contents and thicker oxide thickness. In the 1100 and 1200°C samples, the Sn segregation line was easily detected for the Zircaloy-4 claddings [3,4,5]. But the line could not be detected in the oxide layers of HANA-4 claddings.

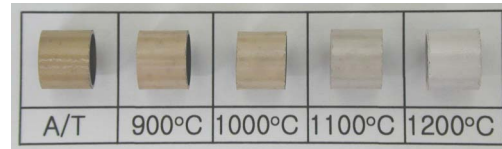


Fig. 2 Appearances of HANA-4 (600 ppm H/80 μ m OT)

4. Conclusions

1. The oxidation kinetics of the simultaneously hydrided/oxidized HANA-4 claddings was obeyed by the parabolic rate at 900 to 1200°C.
2. The oxidation resistance of HANA-4 claddings was better than the Zircaloy-4 claddings
3. The pre-formed hydride/oxide reduced the parabolic rate constant due to the previous denser oxide layer.
4. The colors of the hydrided/oxidized HANA-4 and Zircaloy-4 were changed from the brown to gray as the oxidation temperature increased.
5. The Sn segregation line in the Zircaloy-4 oxide layers was easily detected at 1100 and 1200°C but was not detected in the oxide layers of HANA-4.

ACKNOWLEDGEMENT

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