The Influence of Fluorine on the Breakaway phenomenon of Zr-alloy

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1. Introduction

Loss of the coolant accident (LOCA) is one of the most important design-based accidents when concerning the behavior of a fuel cladding. During a typical LOCA condition, the fuel cladding balloons due to increasing fuel oxidation temperature and internal pressure [1-3]. Finally the cladding might be severely oxidized by a high temperature steam environment and lose ductility by high temperature oxidation. As the time increased at specific temperature, it was observed a breakaway oxidation which a sudden or `cat-astrophic` increase of the oxidation rate. It is investigated the effects of fluorine on the breakaway oxidation properties of Zr-based alloys. The fluorine in the Zr-based alloys is considered important factor since it affects on breakaway of the fuel claddings. Although some researches have reported on the effect of a fluorine in the Zr-based alloys on a steam oxidation at LOCA temperature, a detailed understanding of the effects has not be found as yet. The breakaway oxidation phenomenon in Zr-based alloys were studied in the temperature of 1000℃ for up to 3840s by using a LOCA-simulated test. It anticipated that the breakaway time was shortened by the effect of fluorine polluted on the surface.

2. Experimental procedure

The chemical composition of the cladding used in this study is shown in Table1.

Sn	Fe	Cr	Zr
1.35	0.2	0.1	Bal.

Table 1. Chemical compositions of Zircaloy-4

Two kinds of samples were used in this study. The first one was as-received Zry-4. The other was Zry-4 cladding with the surface treatment by using the HF solution. Fig. 1 shows an illustration of LOCA test scheme and cooling sequence. As-received Zry-4 and Zry-4 cladding with the surface treatment by using the HF solution were oxidized at the temperature of 1000℃ by using LOCA-simulated test. And it was by air cooled from 1000℃ to the intermediate temperature of 800 ℃ and then water quenching at test temperature of 800℃. The duration time was from 480 to 3840 sec. The steam supply rate was 0.6g/cm^2 min (STP) at 1 atm. This steam flow rate was adequate enough to satisfy the conditions for a high-temperature oxidation between the steam and the Zr claddings without a steam starvation on the basis of a review of previous literatures[4,5]. The cladding samples were cut into 50mm in length and were ground carefully for the cut area up to Grit No. 1200 of SiC paper, and then the fluorine sample was pickled in a solution of 5 % HF, 45 %HNO_3 and 50 %H_2O and dipped in water for 60 sec after pickled and cleaned ultrasonically in an ethanol and acetone solution. The optical microscope was used to observe the microstructural characteristics of the ZrO_2 phase, the oxygen stabilized α-Zr layer and and prior β-phase region with the test conditions.

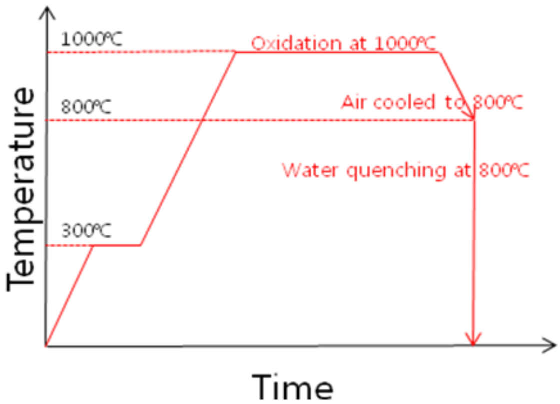

Fig. 1 Illustration of the LOCA-simulated oxidation and water quenching test scheme

3. Results and Discussion

3.1. Oxidation behavior

Fig.2 shows the oxidation behaviors of the Zircaloy-4 cladding with the surface treatment by using the HF solution and as-received zry-4 tested at 1000^{o}C of the steam flow environment. The oxidation behaviors of the both specimens for an exposure time of less than 2400s obeyed the parabolic rate law, which is general trend during a high-temperature oxidation of Zr alloys under a steam atmosphere at that temperature. In the exposure time up to 3840s, the weight gain of the specimen increased monotonously. The breakaway oxidation of the as-received zry-4 occurred after an exposure for about 3360s. But breakaway oxidation time of the F specimen was about 2880s. It is possible to suppose that the breakaway oxidation behavior would be influenced by the surface treatment by using the HF solution on the Zr alloys.

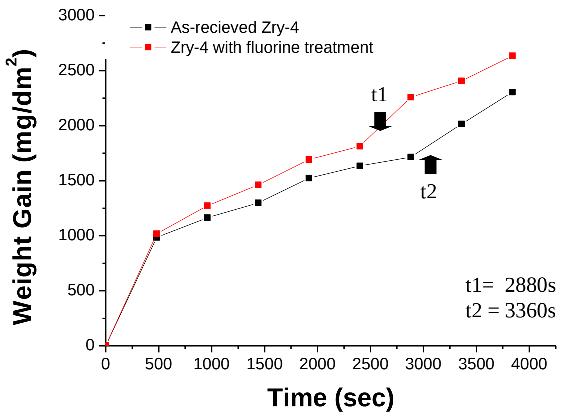

Fig. 2 Oxidation behaviors of as-received Zry-4 and Zry-4 with the surface treatment by using the HF solution at 1000 ^{o}C for 3840sec

3.2. microstructures

Fig.3. shows the oxide layer of the Zry-4 cladding with the surface treatment by using the HF solution and as-received zry-4 tested at 1000^{o}C of the steam flow environment.

(a)

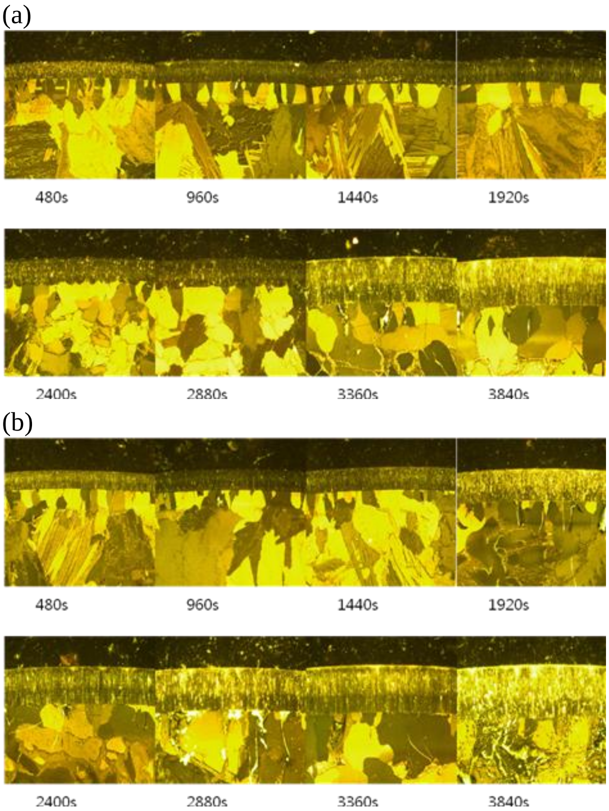

Fig. 3 Optical micrographs of oxide layers formed on Zry-4 alloys at 1000^{o}C from 480 to 3840s; (a)As-received Zry-4 (b) Zry-4 with the surface treatment by using the HF solution

The oxide layer of the as-received Zry-4 cladding increased consecutively. But the oxide layer was abruptly increased from 3360s. At a glance, from Fig3(a), the precursor to breakaway oxidation was the transition from a "flat" oxide metal interface to a wavy inter face. After the transition, cracking of the weak oxide occurred and then the weight gain rate was increased by cracking. The oxide layer of the Zry-4 cladding with the surface treatment by using the HF solution was almost the same from the as-received Zry-4 for the various exposures. However, oxide layer of the Zry-4 cladding with the surface treatment by using the HF solution was abruptly increased with no transition from a "flat" oxide metal interface to a wavy interface at the early stage. Consequently, the effect of the surface treatment by using the HF solution is the most important factor to cause breakaway oxidation. And it anticipated that the breakaway oxidation occurred continually by difference of surface treatment on the cladding surface.

4. Conclusions

The high temperature oxidation of Zircaloy-4 cladding with fluorine was investigated. The influence of fluorine on the high-temperature oxidation behavior was found to be a significant factor to cause breakaway oxidation. Fluorine on the surface of the Zry-4 caused breakaway oxidation at early time and sudden increase of the weight gain than as-received Zry-4

ACKNOWLEDGEME REFERENCES

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