Effect of fluorine on the breakaway oxidation properties 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 temperature and internal pressure [1-3]. And then 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 [3]. The fluorine on the Zr-based alloys is considered important factor since it considerably 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. After preparing for the cladding with different fluorine on a surface of the Zr-based alloys, The breakaway oxidation phenomenon was studied in the temperature of 1000℃ for up to 10080s by using a modified thermo-gravimetric analyzer(TGA). This work is focused on the breakaway occurrance with test time by using the insuit measuring technique.

2. Experimental procedure

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

Table 1. Chemical compositions of Zircaloy-4

Chemical Composition, wt.%				
Nb	**Sn**	**Fe**	**Cr**	**Zr**
-	1.35	0.2	0.1	Bal.

The Cladding type samples were cut into 8mm in length and were ground carefully for the cut area up to Grit No. 1200 of SiC paper, and then the HF1 sample was just dried in the hood after pickled. The HF2 sample was dipped in water for 60 sec after pickled and then dried it in the hood. The HF3 sample was pickled in a solution of 5 % HF, 45 % HNO_3 and 50 %H_2O and cleaned ultrasonically in an ethanol and acetone solution. This method is to control the fluorine on Zr-cladding surface. Fluorine contamination is increased from HF1 to HF3 samples. Oxidation test in steam were conducted by using thermo-gravimetric analyzer at 1000℃[4]. The duration time was up to 10080 sec. The microstructure and oxide layer observation were performed by using optical microscope (OM).

3. Results and Discussion

3.1. Oxidation behavior

Fig.1 shows the oxidation behaviors of the Zircaloy-4 cladding with the surface treatment by using the HF solution tested at 1000°C. The oxidation behaviors for an exposure time of less than 900s obeyed the parabolic rate law, which is general trend during a high-temperature oxidation of Zr alloys under a steam atmosphere at that temperature. From 900s, the weight gain of the specimen didn`t follow a general rate law such as parabolic rate law, cubic rate law. The breakaway oxidation behavior of both HF1 and HF2 specimens occurred. No breakaway oxidation behavior in HF3 specimens were detected up to the end of time at 1000C. Although the weight gain of HF3 is higher than HF1, HF2 in early stage of high temperature oxidation, the weight gains of both HF1 and HF2 were dramatically increased after breakaway point. 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.

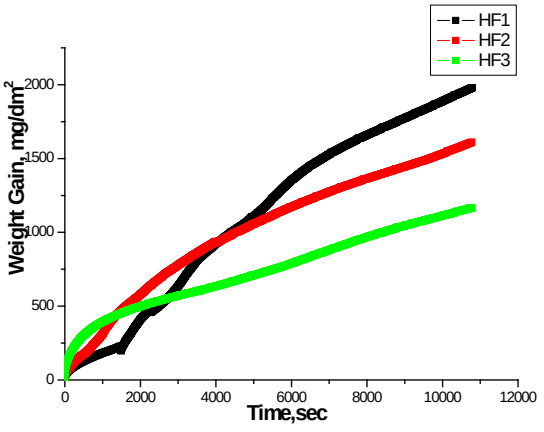

Fig. 1. Oxidation behaviors of Zry-4 with the surface treatment by using the HF solution at 1000 °C for 10080sec

Fig.2. shows the oxidation behaviors of HF1 and HF2 samples to check the reproduction of fluorine contamination. In the case of HF2, the results of repeated experiment indicated no breakaway oxidation same as the first experiment. But in the case of HF1, although the results of repeated experiment had a little different when compared to the first experiment, it was observed that the breakaway oxidation occurred consecutively. The first breakaway oxidation occurred at about 200 mg/dm^2, the second breakaway oxidation occurred at about 550 mg/dm^2, and the third breakaway oxidation occurred at about 1500 mg/dm^2. Consequently, the effect of the surface treatment by using the HF solution is an important factor to cause breakaway oxidation. And it anticipated that the breakaway oxidation occurred continually by difference of surface treatment on the cladding surface.

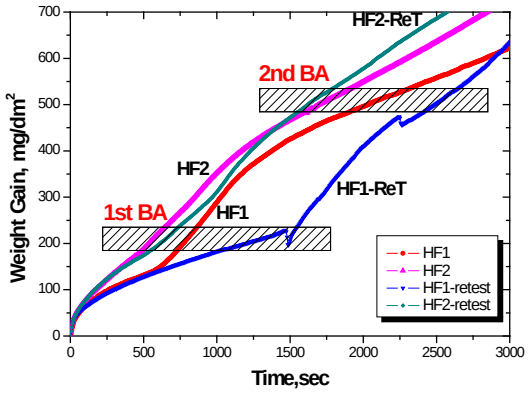

Fig.2. Oxidation behaviors of HF1 and HF2 alloys in 1000 °C steam

3.2 Surface appearances

After the oxidation tests at 1000°C, the surface appearances were observed for the claddings with the surface treatment by using the HF solution, as shown in Fig. 3. The surface colors were changed from a dark black to a gray color with increasing the oxidation time.

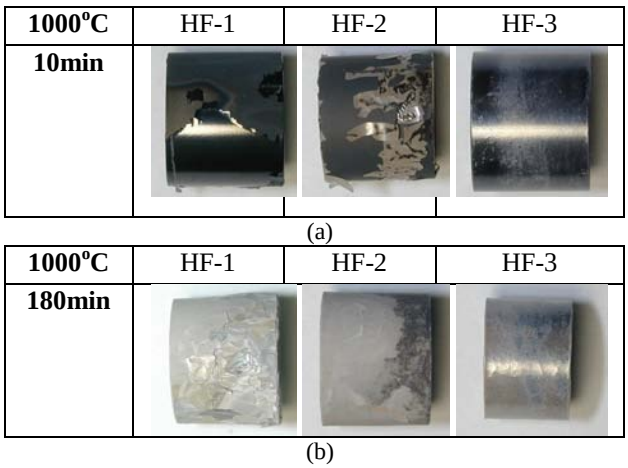

Fig.3. Surface appearances after the oxidation tests at temperatures of 1000 °C : (a)10min (b)180min

4. Conclusions

The high temperature oxidation of Zircaloy-4 cladding with fluorine treatment on surface was investigated. The influence of fluorine on the high-temperature oxidation behavior was found to be a significant factor to cause breakaway oxidation. As fluorine contents increased, Breakaway oxidation occurred consecutively. And the surface colors were changed from a dark black to a gray color with increasing the oxidation time. HF1 treated by using HF solution was more oxidized and surface appearance was more white than other samples for same oxidation time at 1000 °C.

ACKNOWLEDGEME

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