High-temperature oxidation accelerated effects of Zircaloy by hydride

Sungwoo Ha[a], Kwangheon Park[a]*, Yunmock Jung[b]
[a]Department of Nuclear Engineering, Kyunghee University, Kyunggi-do 776-701, Korea
[b]Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon

1. Introduction

Nuclear fuel cladding should be durable to corrosion and transformation so that it can endure in case of being exposed to a high-temperature/high-pressure environment, as well as to a high-radiation environment, for long hours. At the same time, it should require a small neutron absorption cross-section and superior heat conductivity. Recently, the operation method of nuclear reactors has become high burn-up and long-period, which increases the possibility of nuclear fuel cladding damage. Oxidation acceleration of Zircaloy cladding is one of the major factors that restrict performance of the high burn-up fuel rod, as it increases the damage frequency of nuclear fuel cladding. Zircaloy generates an oxidized layer and creates hydrogen as it reacts with high-temperature water. Although most of this created hydrogen is released as coolant, approximately 10~20% of hydrogen melts inside the cladding. The hydrogen that melts into the interior of the cladding during normal conditions can rapidly accelerate oxidation in accidents, resulting in a fatal impact on securing safety. The most important impact that hydrogen absorbed under normal conditions has on nuclear fuel cladding in the case of a LOCA occurrence is the breakaway oxidation phenomenon. Following the trend of high burn-up and long-period nuclear fuel cladding, the burning environment is becoming more and more severe. Hence, continuous studies on the impact of hydrogen on nuclear fuel cladding are required.

2. Methods and Results

2.1 Experiment equipment and methods

Before conducting high-temperature oxidation (950°C, 1,000°C), the specimen was prepared such that approximately 200 wppm of hydrogen was artificially inserted inside the Zircaloy, for the purpose of evaluating the impact of hydrogen absorbed inside cladding on high-temperature oxidation.

Make hydride layer on the sample surface, using cathodic hydrogen charging method. By using an electric furnace, maintain the vacuum heat treatment for hydrogen in the hydride layer formed homogeneously. hydrogen charging procedure was conducted in accordance with the procedures of the zirconium alloy hydrogen charging of KAERI. After the heat treatment, analyzed amount of charging hydrogen in the zircaloy by vacuum melting method.

As for the experiment equipment for the high-temperature continuous measurement oxidation equipment (TGA) was used to measure the weight change from oxidation in real time by using microbalance, which is able to detect as small as a 0.1-μg change in the specimen (Figure 1).

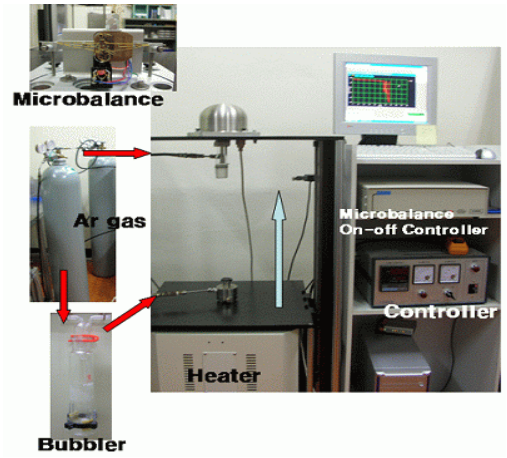

Fig 1. High-temperature continuous measurement oxidation equipment (TGA)

Discontinuous measurement oxidation equipment (tube furnace) was used, which can support oxidation experiments on multiple specimens under identical conditions, although it is unable to measure continuous weight change (Figure 2).

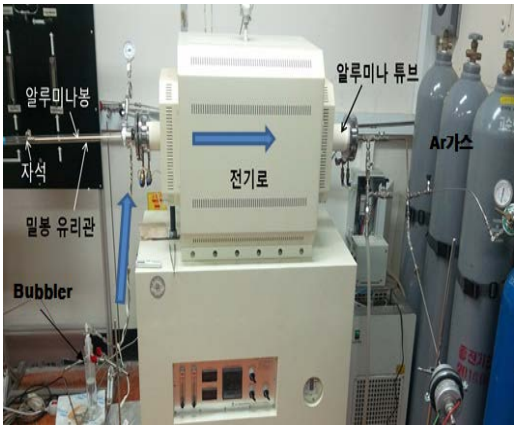

Fig 2. High-temperature discontinuous measurement oxidation equipment (tube furnace)

2.2 Experiment results

In atmospheric pressure and steam atmosphere, the Zry-4 cladding with hydrogen insertion and normal Zry-4 cladding were oxidized under high-temperature (950°C, 1,000°C) and steam conditions for a long interval (6,000 seconds). As a result, breakaway oxidation occurred and the hydrogen oxidation acceleration phenomenon, which was not observed within 1,000 seconds, took place once the breakaway oxidation began. That is, the weight gain difference between oxidation acceleration was observed where the Zry-4 cladding with hydrogen insertion and normal Zry-4 began to increase. Based on this, we can say that the hydrogen inserted inside the cladding played a role as an accelerating factor of oxidation once the breakaway oxidation was initiated. As shown in Figure 3, Figure 4 breakaway oxidation took place at approximately 3,687 seconds at 950°C and 2,860 seconds at 1,000°C.

The weight gain difference increased until approximately 5,000 seconds after the breakaway oxidation, but stayed the same or even decreased afterward. This is because the oxidized layer's volume had increased and Zircaloy's metal layer had decreased due to the continuous oxidation. This eventually slowed down the speed of hydrogen's absorption into the cladding.

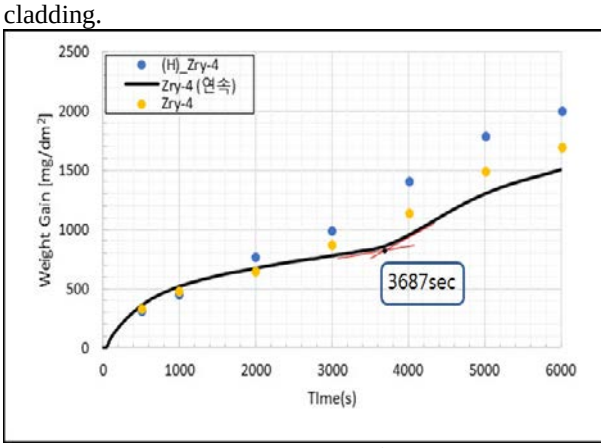

Fig 3. Oxidation experiment results of Zry-4 at 950°C°C in atmospheric pressure and steam atmosphere

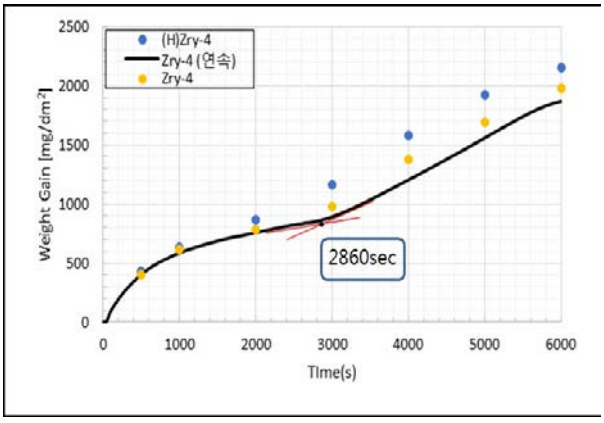

Fig 4. Oxidation experiment results of Zry-4 at 1000°C in atmospheric pressure and steam atmosphere

Hydrogen can also exist in the α layer and residual β layer of Zircaloy metal, in addition to the oxidized layer. As oxidation proceeded, absorption rate of hydrogen slowed down following the increased size of the oxidized layer and the relatively smaller size of the metal layer (Figure 5).

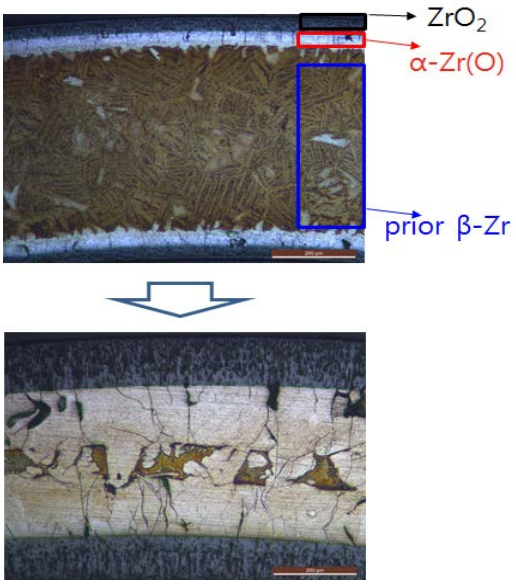

Fig 5. Growth in oxidized layer during Zircaloy oxidation

The microstructure under each experiment condition is presented in Figure 6 and Figure 7. OM analysis results also confirmed that the oxidized-layer size of the Zry-4 cladding with hydrogen insertion was larger than that of the normal Zry-4 cladding. Moreover, cracks were not observed, unlike in the previous oxidation experiment performed under high-pressure and steam conditions. Based on this, we can say that the oxidized layer created in atmospheric pressure and steam atmosphere has greater resistance against hydrogen absorbed inside the cladding, compared to the layer created in the high-pressure and steam atmosphere.

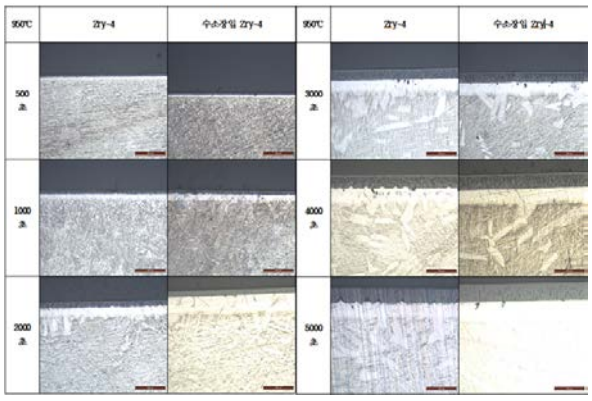

Fig 6. The microstructure of Zry-4 cladding in atmospheric pressure and steam atmosphere at 950°C (OM)

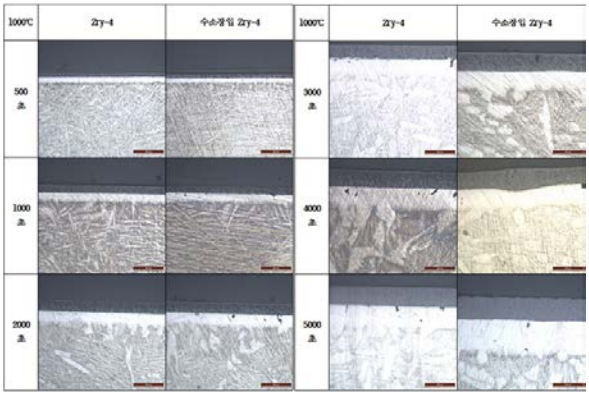

Fig 7. The microstructure of Zry-4 cladding in atmospheric pressure and steam atmosphere at 1,000℃ (OM)

The minimum time of breakaway oxidation observed in this study was compared with those in other study results (Table 1).

Table 1. Comparison of minimum time of breakaway oxidation with other study results

	This study	Baek[1]	S.Leistikow[3]	AREVA[4]
Zircaloy-4	2,860sec	3,100sec	2,400sec	5,000sec

There were large differences between the observed minimum time of breakaway oxidation in this study and those from other study results. These differences can be attributed to Zry-4's dimensions, surface roughness, abrasion, surface finish, etc. Defects or damage on the cladding surface can create geometric discontinuity inside the cladding, affecting stress conditions in the oxidized layer or the layer interface between Zircaloy and oxidized layers. Moreover, the cleansing or etching process also differs. The hydrofluoric solution used during the etching process has a critical role in determining the minimum time of breakaway oxidation [2].

3. Conclusions

In high-temperature oxidation in atmospheric pressure and steam atmosphere, oxidation acceleration due to inserted hydrogen was not observed until the beginning of breakaway oxidation.

However, oxidation of Zry-4 cladding where hydrogen was inserted was accelerated after the breakaway oxidation started. As for the impact of absorbed hydrogen, tetragonal crystals from the oxidized layer created in the metal boundary layer are transformed into monoclinic crystals due to relaxing stress following the gradual growth of the oxidized layer.

In the case of no hydrogen, they are transformed into a columnar monoclinic crystal oxidized layer that has superior corrosion resistance. However, in the case of high contents of hydrogen, the hydrogen decreases the surface energy of the monoclinic crystals to create an equiaxial monoclinic crystal oxidized layer that is unstable against stress. Moreover, cracks appear in the equiaxial oxidized layer due to the surrounding stress.

Hence, corrosion resistance decreases, eventually accelerating oxidation. These study results imply that cladding can be fractured by brittleness even in the case of ECR less than 17%, which was enacted in 1973. They also indicate that it is necessary to reconsider the previous ECR of 17% in current situations in which the operation of a nuclear plant has become high burn-up and long-period. Moreover, the study results are expected to be used as fundamental data for setting the minimum beginning of breakaway oxidation that is required by NRC.

REFERENCES

[1] Jong Hyuk Baek, and Yong Hwan Jeong, Breakaway Phenomenon of Zr-based Alloys during a High-Temperature Oxidation, Journal of Nuclear Materials, Vol.372, p.152-159 (2008)

[2] 이기원, Breakaway 현상에 미치는 핵연료 피복관의 표면 상태효과, 석사학위논문, 충남대학교 (2011)

[3] S. Leistikow and G.Schanz, Oxidation kinetics and related phenomena of zircaloy-4 fuel cladding exposed to high temperature steam and hydrogen-steam mixtures under PWR accident conditions, Nuclear Engineering and Design, Vol.103, p.65-84 (1987)

[4] U. S. Nuclear Regulatory Commission, Cladding Embrittlement during Postulated Loss-of-Coolant Accidents, NUREG/CR-6967 (2008)