High Temperature Oxidation Behavior of Hydrogen-Charged Zirconium Alloy under High Steam Pressure

Yeonseung Kim[a] , Seongwoo Yang[a], Kwangheon Park[a *] , Seungjae Lee[b], Sundoo Kim[b]
[a]*Green Nuclear Research Lab., Global Campus, Kyunghee University, 446-701*
[b]*Korea Nuclear Fuel, Yuseong, Daefeon, 305-353*
**Corresponding author : kpark@khu.ac.kr*

1. Introduction

Since 1990, improving fuel cycle economy has required an extension of the fuel cycle and higher burn-up operation. The modern PWR tend to be operated in the severe operating conditions[1]. Moreover, hydrogen from the dissociation of water molecules during oxidation process can be absorbed in Zirconium alloys resulting in hydrogen embrittlement [2].

To date, some systematical research has been conducted regarding hydrogen behavior in Zirconium alloy, including hydrogen absorption and embrittlement. This research indicated that hydrogen absorption has no great influence on the oxidation of cladding at LOCA (Loss of Coolant Accident) [3]. However, most of these studies considered only oxidation temperature and time, regardless of the effect of hydride precipitation under high steam pressure. Therefore, this study investigated the oxidation behavior of hydrogen charged Zirconium alloy cladding under high temperature and high steam pressure.

This data will give an exact evaluation of the corrosion of fuel cladding. The results can also be used to prevent the problems arising from hydride precipitation in the nuclear fuel cladding materials.

2. Experimental

2.1 hydrogen charge

A gaseous hydrogen charging method was used for creating specimens in this study. Hydrogen was charged into the specimen when pure hydrogen flowed on the specimen surface. This method's strong point is accurate charge. It is necessary to vacuum equipment.

2.2 Specimen

The specimens used in this study are low-Sn Zircaloy-4 and Nb-added alloy (Zirlo) tubes which are used in commercial nuclear power plants. Cladding tubes were cut to the height of 6 mm~7 mm. They were ground, polished, pickled, and cleaned.

Table 1. Shows the chemical composition of the specimens used in this study.

Table 1. Chemical composition of specimens

	Zr	Sn	Nb	Fe	Cr	O	N	Ni
low-Sn Zry-4	base	1.35	.	0.2	0.1	0.12	<0.0008	<0.007
Zirlo	base	1.0	1.0	0.1	.	0.12	.	.

2.3 Apparatus and Experimental method

Fig. 1 shows the apparatus for high temperature oxidation under high steam pressure. The test apparatus is composed of a high pressure vessel and two heaters. The outside heater enhances the steam pressure by boiling, and the inside heater directly controls the specimen's temperature.

After the pickled specimen was located in the test position, the pressure vessel was dropped and sealed. Distilled water was put into the test apparatus, and the steam pressure was enhanced by heating.

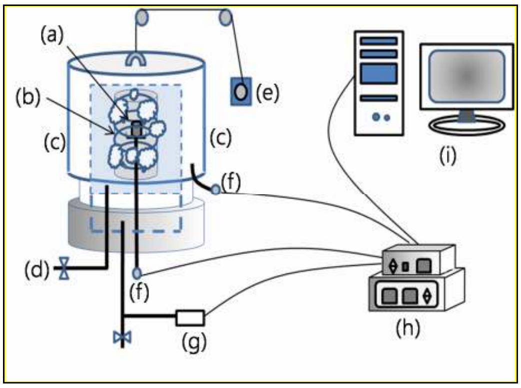

Fig. 1. Apparatus for high temperature oxidation under high steam pressure
(a) Specimen (b) Inner heater (c) Outer heater
(d) Steam vent (e) Lifting motor (f) Thermocouple
(g) Pressure sensor (h) Controller (i) Computer recording

Initial interior gas (air) was discharged before the test since air could affect the oxidation amount. The specimen's temperature was held below 400 ℃ until reaching the desired steam pressure. After the steam pressure had reached its target, the specimen's temperature was increased to the target temperature and the specimen was oxidized at the target time.

The specimen then was cooled to room temperature and pulled out, and its weight gain was measured. Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) were used to observe the specimen's oxide layer and microscopic structure.

The target temperature range was from 700 ℃ to 900 ℃, the steam pressure was from 0.1 MPa to 10.0 MPa, and the hydrogen concentration was from 300 ppm to 800 ppm. The oxidation time was controlled at 1000-2000 sec.

3. Result and discussion

Fig. 2 shows the hydrides on the surface of hydrogen charged low-Sn Zircaloy-4. Hydrides were inhomogeneously distributed throughout the surface. Therefore, the oxidation will be partially generated.

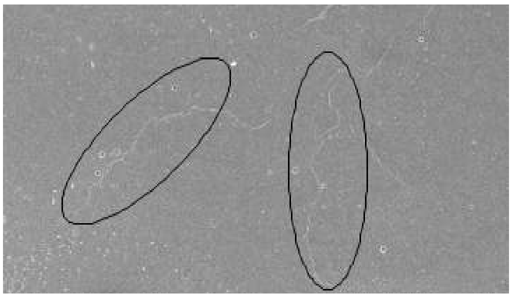

Fig. 2. SEM image of surface of hydrogen charged low-Sn Zircaloy-4 (300 ppm)

Fig. 3 shows the weight gain of specimens at 800 ℃. An acceleration of oxidation was detected under high steam pressure and high temperature. As well, hydrogen-charged low-Sn Zircaloy-4 oxidation was boosted in the high hydrogen concentration. Therefore, pressurized steam and hydrogen concentration must be considered for correct evaluation of oxidation. However, acceleration of oxidation by pressurized steam and hydrogen concentration was not observed in Zirlo, an Nb-added alloy. It is known that Zirlo has corrosion resistance in a high burn-up environment [4].

Results on the as-received Zirlo show larger weight gain than that in low-Sn Zircaloy-4 at low pressure, but the gain gradually becomes less than low-Sn Zircaloy-4 as steam pressure rises.

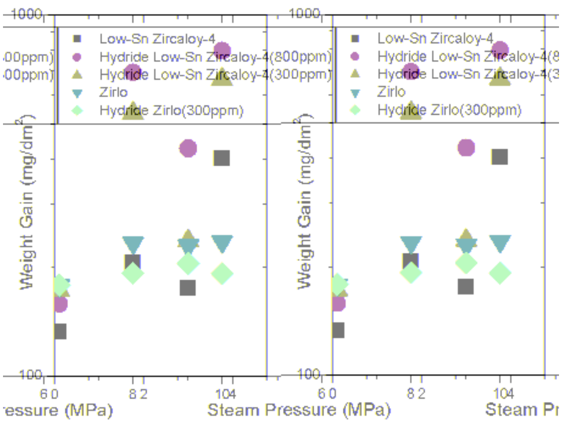

Fig. 3. Weight gain of Zirconium alloys (800 ℃)

In contrast with the oxide layer formed under atmospheric steam pressure when the as-received specimen was used, many cracks were observed in the oxide layer formed under high steam pressure and high hydrogen concentration. (Fig. 4)

In the oxide layer of as-received low-Sn Zircaloy-4 many horizontal cracks were observed under high temperature and high steam pressure conditions. Also, in the oxide layer of hydrogen charged low-Sn Zircaloy-4 many horizontal cracks and vertical cracks were observed due to a high hydrogen concentration. (Fig. 5)

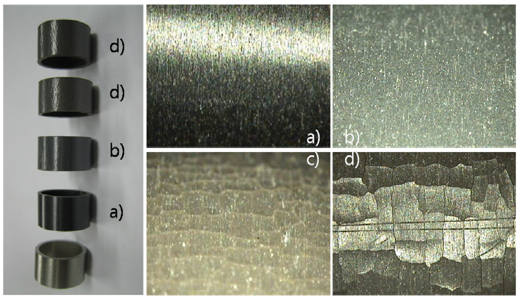

Fig. 4. Surface of hydrogen charged low-Sn Zircaloy-4 (800 ℃, 300 ppm)
(a) 0.1 MPa (b) 3.0 Mpa (c) 8.0 MPa (d) 10.0 MPa

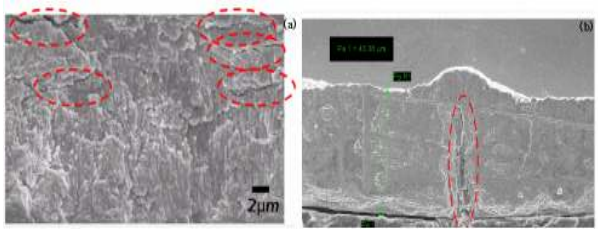

Fig. 5. SEM image of oxide layer of low-Sn Zircaloy-4 (800 ℃, 10.0 MPa)
(a) As-received specimen
(b) Hydrogen charged low-Sn Zircaloy-4 (300 ppm)

4. Conclusion

An effect of hydride precipitation of low-Sn Zircaloy-4 was detected. Many cracks in the oxide layer were detected at high temperature, high steam pressure, and high hydrogen concentration. Nb-added alloy has little or no effect on high steam pressure and high hydrogen concentration. Addition of Nb is known to increase the corrosion resistance. Therefore, these results show Zirlo is more effective than low-Sn Zircaloy-4 at LOCA.

Acknowledgment

We would like to express our appreciation to Korea Nuclear Fuel (KNF) for the financial support of this study. Also this work was financially supported by MOCIE through the EIRC program.

REFERENCES

[1] A. Jonsson, L. Hallstadius, B. Grapen-giesser, and G Lysell, Fuel for the 90's : ANS/ENS International Topical Meeting on LWR Fuel Performance, Avignon, France, 1991.
[2] K. S. Lee, Study on The Hydrogen Behavior of Zr-based Alloy, GOVP1200132597, 2001.
[3] J. H. Lee, Deformation and embrittlement behavior of zirconium fuel cladding under simulated LOCA condition, Chungnam National University. Korea, 2004
[4] H. G. Kim, Phase Transformation and Oxidation Characteristics of Zr-Nb Alloys, Dept. of Metallurgical Eng, Yonsei University, 2004