

## The effect of dissolved hydrogen on the high pressure steam oxidation of Zircaloy-4

Seonggi Jeong<sup>a</sup>, Kwangheon Park<sup>a\*</sup>

<sup>a</sup>Department of Nuclear Engineering, Kyunghee University, Kyunggi-do, 446-701

\*Corresponding author: kpark@khu.ac.kr

### 1. Introduction

Zr-alloys have been used as a cladding material for the nuclear fuel for several decades. The cladding is the first barrier against the release of radioactive fission products to the outside. The behaviors of the cladding under the accidental conditions have to be well analyzed, since the safety of nuclear power plants becomes one of main issues after Fukushima accident. Hydrogen is generated from the oxidation of the cladding by water and dissolves into the cladding during operation. The dissolved hydrogen becomes hydrides when the concentration of hydrogen exceeds the solubility limit at low temperatures. Due to the quite different mechanical properties of the hydride, the effect of hydrides on the maintenance of the fuel during operation and storage has been main concerns. However, the dissolved hydrogen also affects high temperature oxidation, even though the hydrogen is fully dissolved into the matrix at high temperatures (above 700C). In this study, we observed the effect of dissolved hydrogen on the high pressures steam oxidation of Zry-4 claddings.

### 2. Experimental

#### 2.1 Specimen preparation

The specimens used in this study are Zircaloy-4 (Zry-4) tubes used in commercial nuclear power plants. Table 1 shows the chemical composition of Zry-4. Zry-4 tubes were charged with hydrogen up to 800ppm. Cladding tubes were cut to the height of 5mm, then, they were polished, pickled, and cleaned.

Table 1. Chemical composition of specimen

	Zr (wt%)	Nb (wt%)	Sn (wt%)	Fe (wt%)	Cr (wt%)
Zry-4	bal.	-	1.35	0.2	0.1

#### 2.2 Apparatus and Experimental Method

Figure 1 shows the experimental apparatus used in this study. The apparatus can oxidize a specimen uniformly in steam at pressures from 0.1 to 15.0MPa. The system consists of two vessels and two resistance heaters. The outer vessel is used for maintaining high-pressure steam during the experiment. It is heated up to 400 °C, and the steam pressure is controlled by the amount of water inside.

After the stabilization of steam pressure, the resistance heater surrounding the specimen inside the inner vessel turns on. The specimen is heated to the set-up temperature for the fixed duration of time. After oxidation, we let the specimen cooled and then recovered. We measured the weight increase due to oxidation. We analyzed the microstructures of specimens by an optical microscope.

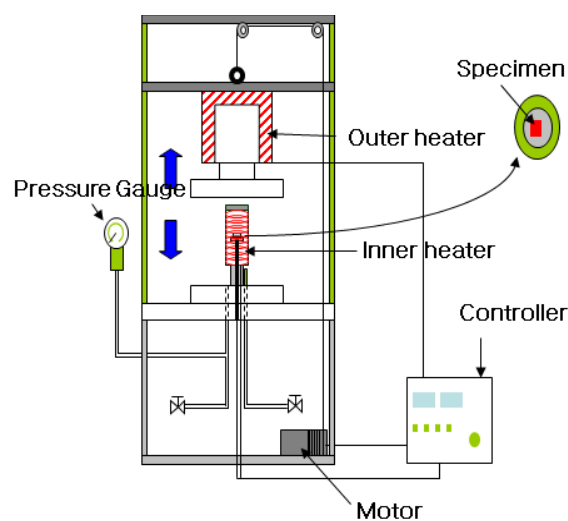


Figure 1. The apparatus used in the experiment.

### 3. Results

Figure 2 shows the result of the weight gain of Zry-4 specimens containing 800ppm of hydrogen and those of normal (hydrogen free) Zry-4 specimens at 800C. High pressure steam enhanced the oxidation of both normal and hydrogen-containing specimens. The enhancement of oxidation by high-pressure steam was more severe to the specimen containing hydrogen. The enhancement of weight gain by steam can be obtained as,

$$\Delta W = 123 \cdot e^{0.011 \cdot P(\text{bar})} \quad \text{: for H-free Zry-4}$$

$$\Delta W = 124 \cdot e^{0.018 \cdot P(\text{bar})} \quad \text{: for H-dissolved Zry-4}$$

About 63% increase of enhancement factor (i.e., from 0.011 to 0.018) was measured by the dissolved hydrogen.

At 800C, the hydrogen of 800ppm fully dissolves into Zry-4 cladding matrix. Hence, the increased enhancement was due to the hydrogen dissolved.

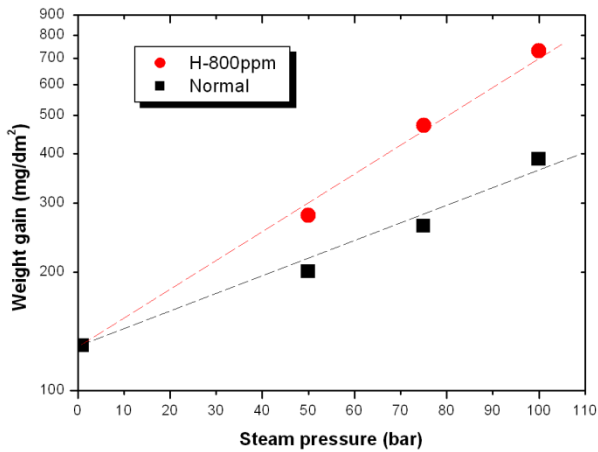


Figure 2. Weight gain by high pressure steam in H-free (normal) and hydrogen dissolved Zry-4 specimens.

Temperature and oxidation time were 800C and 1500sec, respectively.

The weight gain of the H-containing specimen with respect to the oxidation time was evaluated. Figure 3 shows the result. The time dependence of weight gain can be expressed as the following equation.

$$\Delta W = k \cdot t^n$$

The value of n at each steam pressure was obtained from the result.

Pressure (bar)	n
50	0.7
75	1.1
100	0.6

The value of n is about 0.6~1.1 which indicates that the parabolic weight gain law might work in estimating the weight gain of H dissolved Zry-4 cladding.

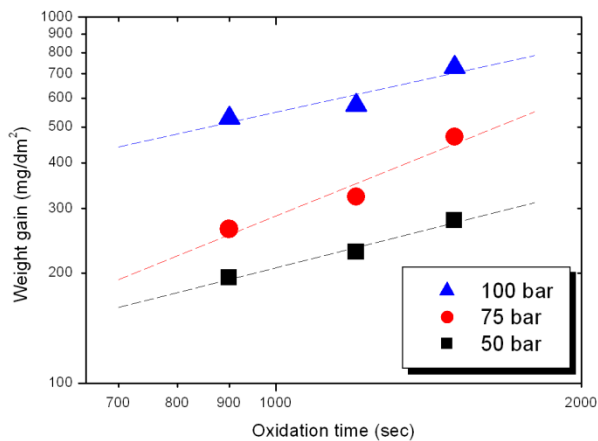


Figure 3. Weight gain of H containing specimens with respect to time at different steam pressure. The temperature was 800C.

The microstructures of the H-dissolved Zry-4 specimens after the oxidation test are shown in figure 4. The oxide layer was not uniform if the specimen was oxidized at high pressure steam. As steam pressure increased, the oxide contained large vertical (to the surface) cracks.

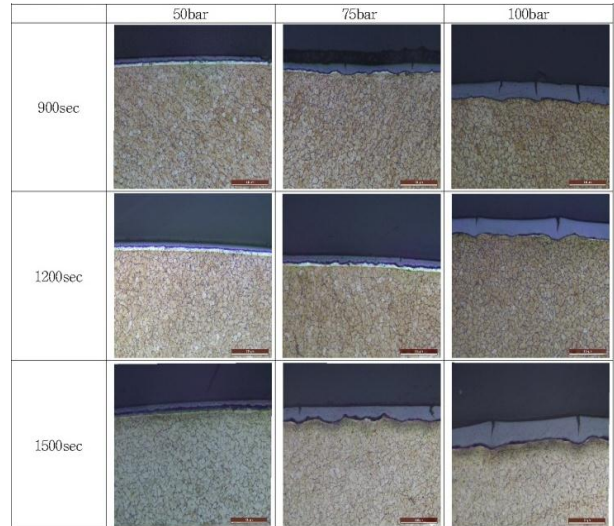


Figure 4. Microstructures of the hydrogen dissolved Zry-4 specimens after high pressure steam oxidation.

#### 4. Discussion and Conclusions

Zry-4 specimens that contain hydrogen also showed the oxidation enhancement by high pressure steam. The extent of enhancement (or enhancement factor) was about 63% higher than hydrogen-free Zry-4 specimens. The role of high pressure steam on oxidation enhancement seems from the formation of non-protective oxide layer. The tetragonal phase near metal layer transforms to the monoclinic oxide as oxide layer grows. High pressure steam somehow affects the transformation resulting in the formation of bad-quality (non-protective) monoclinic oxide. Dissolved hydrogen also affects the transformation by changing the surface energy of newly born monoclinic oxide embryos. Interestingly, the kinetics seems to follow the parabolic rate law (or linear rate law).

#### Acknowledgment

We would like to express their appreciation to National Research Foundation of Korea (NRF) for the financial support of this study.

#### REFERENCES

- [1] B. Cox, Accelerated Oxidation of Zircaloy-2 in Supercritical Steam, AECL-4448, 1973
- [2] R. E. Pawel, J. V. Cathcart, and J. J. Campbell, The Oxidation of Zircaloy-4 at 900 and 1100 in High Pressure Steam, Journal of Nuclear Materials, vol. 82, p. 129, 1979
- [3] K. Park, K. Kim, T. Yoo, and K. Kim, Pressure Effect on High Temperature Steam Oxidation of Zircaloy-4, Metals and Materials International, vol. 7, p.367, 2001
- [4] K. Park, S. Yang, and K. Ho, The Effect of High Pressure Steam on the Oxidation of Low-Sn Zircaloy-4, Journal of Nuclear Materials, vol. 420, p.39, 2012