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

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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. 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℃, 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.

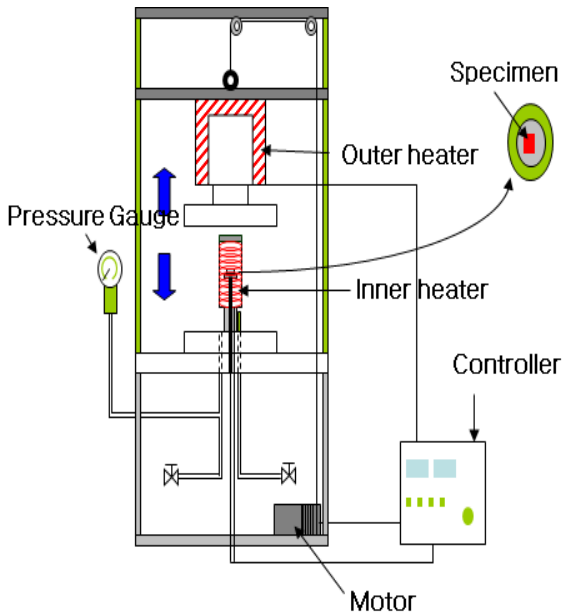

Figure 1 The apparatus used in the experiment.

3. Result

Figure 2. shows the result of the weight gain Zry-4 specimens containing hydrogen and those of normal (hydrogen free) Zry-4 specimens at 800C . 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.

Table 2 The value of n at each steam pressure

Pressure	Dissolved-Hydride	Free-Hydride
50bar	0.7	0.9
75bar	1.2	0.7
100bar	0.6	0.9

The n of free-hydride's value is about 0.7~0.9 which indicates the linear weight gain law. However, the n of dissolved-hydride's value represents the parabolic rate law is about 0.6-1.2

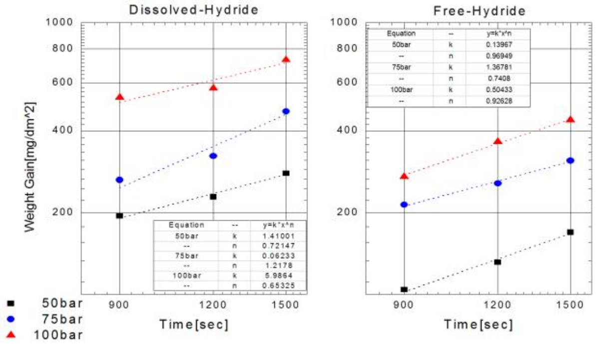

Figure 2 Weight gain of H containing specimens and H free specimens with respect to time at different steam pressure. The temperature was 800C

Figure 3 shows the hydride content of Zry-4 specimens containing 800ppm of hydrogen and those of normal (hydrogen free) Zry-4 specimens at 800C**.** The dissolved-hydride Zry-4 has more hydride contents than normal Zry-4. Furthermore, the content of two different specimens is similar to the weight gain of each pressure conditions.

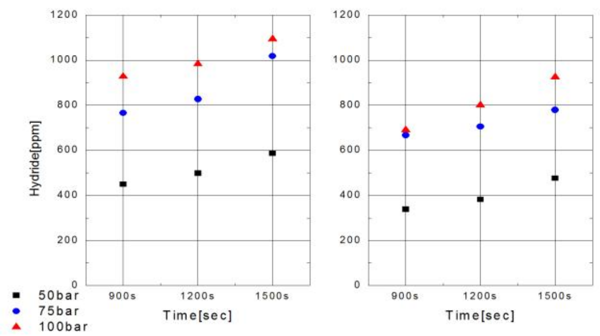

Figure 3. The hydride content with respect to time at different steam pressure.

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.

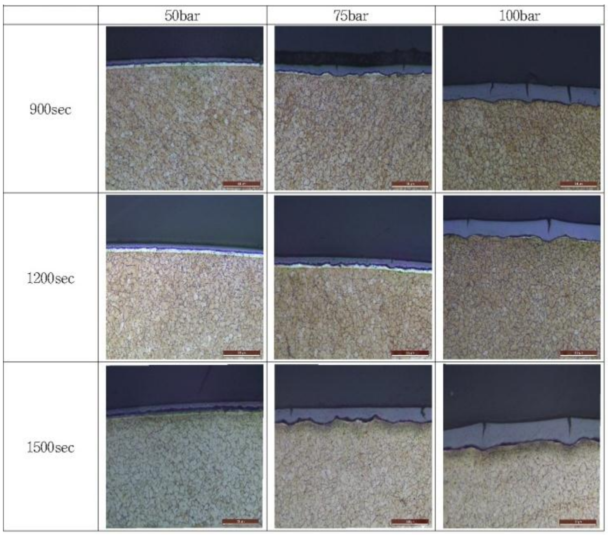

Figure 4. Microstructures of the hydrogen dissolved Zry-4 specimens after high pressure steam oxidation.

4. Discussion and Conclusions

As indicated by the results, dissolved-hydride Zry-4 specimens showed more enhancive weight gain than nomal specimens. The difference of each weight gain is increased by high pressure steam. The role of hydride on oxidation enhancement seems from the formation of non-protective oxide layer. The tetragonal phase transforms to the monoclinic oxide during oxide layer grows. The two phases have to be of good quality for protection. However, Hydride affects the transformation by changing the surface energy of newly born monoclinic oxide embryos. Therefore, non-protective oxide on dissolved-hydride specimens was more increased than normal specimens. Finally, it lead to the enhancement oxidation.

Acknowledgment

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