The effect of Hydride on air oxidation of Zirconium-alloys

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1. Introduction

A loss of the coolant accident is one of the most important design-based accidents when concerning the behavior of a fuel behaviors. Also, as the fuel burn-up increases, corrosion occurs with hydrogen absorption, resulting in degradation of cladding properties. Investigating the effect of the pre-hydride cladding's surface will be of importance. In this study, we measured the oxidation rate of Zircaloy-4, Zirlo, pre-hydride Zircaloy-4 and pre-hydride Zirlo to compare the effect of hydride on the oxidation in air.

2. Experimental

2.1 Specimen preparation

The specimens in this study are Zircaloy-4, Zirlo tubes used in commercial nuclear power plants. Table 1 shows the chemical composition of the specimen. The other specimens are same zirconium-alloys; but were charged with hydrogen up to 800ppm. Cladding tubes were cut to the height of 10mm~11mm and had 2 drilled small holes at the top. 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
Zirlo	bal.	1.0	1.0	0.1	-

2.2 Apparatus and Experimental Method

Thermogravitational method was used. The system consists of an alumina tube surrounded by an electric heater, and gas supply system. The specimen is connected to a platinum wire through holes in it, and is hung to a microbalance mounted above the furnace tube. An electronic heater was able to move up and down. The heater was moved up to the position of the specimen after oxidation temperature was reached. Argon was supplied to the microbalance for the protection of possible damage. The weight gain was measured and recorded continuously to a PC connected to the microbalance. The accuracy of the measurement was about 10ug. The target temperatures were 700℃ 800℃ and 900℃.

3. Results

Weight change by the oxidation in air for each specimen was measured by the microbalance at 700℃ 800℃ and 900℃. Using these weight change measurements, the weight gain per unit area for each specimen was calculated. Sudden changes of weight gain were observed by the spall of oxide film. Pre-hydride specimens showed enhanced oxidation rates, approximately 2 times faster than normal specimens for a given experimental condition. The air oxidation of Zry-4 was the most affected by pre-hydride Zirlo was also heavily oxidized when the specimens were changed with hydrogen. Zirlo itself was not protective in air oxidation compared to Zry-4. Zirlo was known to be better against corrosion in high temperature water. However, the oxidation rate of Zirlo tube was measured to be higher than that of Zry-4. However, Zirlo with hydride in it looked somewhat more protective than Zry-4 with hydride.

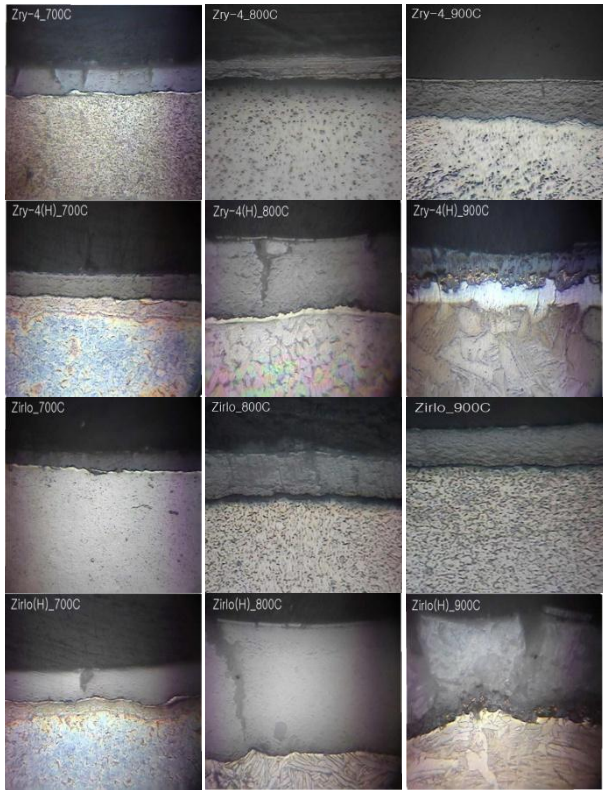

Figure 1. Optical Microscope image of the each specimen

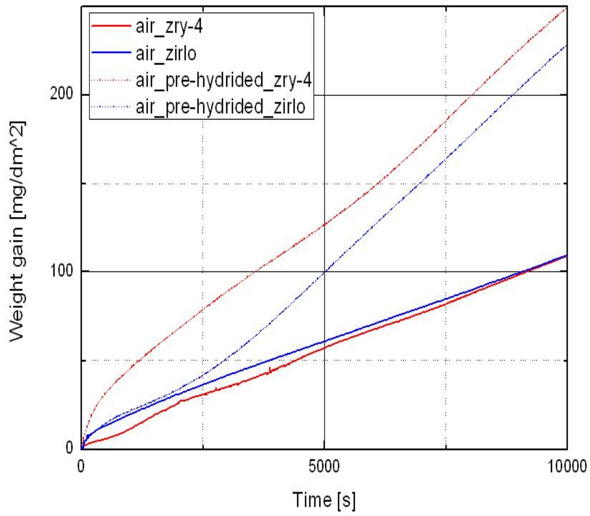

Figure 2. Weight gain of air oxidation at 700℃

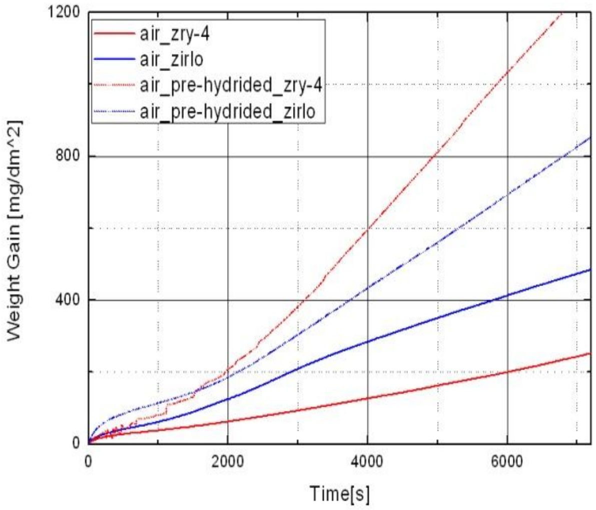

Figure 3. Weight gain of air oxidation at 800℃

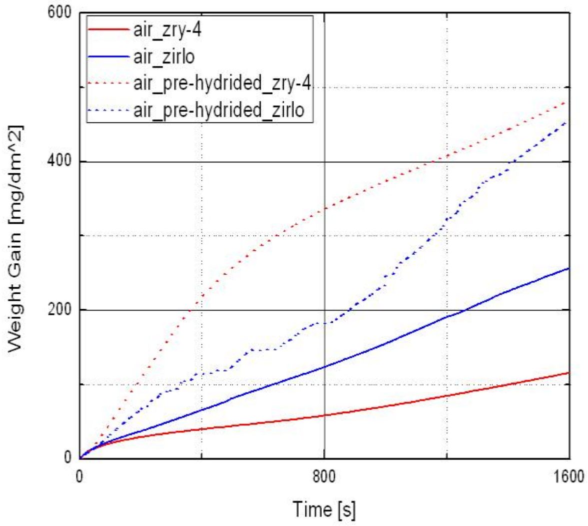

Figure 4. Weight gain of air oxidation at 900℃

4. Discussion and Conclusions

The kinetics of oxidation of zirconium-alloys in air was somewhat different from that in steam. The oxidation rates of both alloys in air are higher than the rates in steam. The main reason for the enhancement of oxidation under the air may be from the formation of nitrides in the metal layer. Generally oxidation rates of Zirlo at high temperatures (above 800℃) are similar or slightly less than those of Zry-4 under the steam. However, Zirlo oxidized faster than Zry-4 in air at these high temperatures. The micro-structure of the oxide layer formed on Zirlo cladding shows more fine microcracks near the metal interface (Fig.1). These microcracks seem fast paths and help for oxygen or oxygen vacancies to move through the oxide layer, resulting in thicker oxide layer. The oxide formed on Zirlo seems to be more fragile or more sensitive to the nitrides than Zry-4, when oxide layer grows into the metal layer. The air oxidation of pre-hydride zirconium-alloys were accelerated by rearranged hydride and more increased than the other zirconium-alloy. Nowadays the high burn-up fuel is emerging interest as the burn-up increasing. Therefore, more examination on the oxidation kinetics of pre-hydride zirconium-alloys is needed for the safety evaluation on the accidents occurs in open air.

Acknowledgment

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