

The effect of dissolved hydrogen on the air oxidation of Zircaloy-4

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1. Introduction

Zirconium alloys have long been used as nuclear fuel cladding material. It's because Zirconium has low thermal neutron absorption, mechanical integrity at high temperatures, and high corrosion resistance in water. Nuclear fuel cladding is the first shield to prevent the spread of radioactive fission materials, so the safety is very important in steady-state and accident conditions as well. Especially, the nuclear fuel cladding behavior should be analyzed very carefully in case of LOCA accidents.

In order to analyze the integrity of the cladding during accidents, the temperature increase due to the reaction (heat) with water vapor and the reduction in the thickness of the metal layer (or oxide film thickness) by oxidation should be found. Especially, the thickness of the oxide layer should be measured accurately to determine whether the transfer of nuclear fuel is possible after the accident. Therefore, studies on the factors affecting the cladding oxidation are very required. Among the factors affecting the oxidation, effect of hydrogen contained in cladding metal has been mentioned recently. In this study, we observed the effect of dissolved hydrogen on the air and steam oxidation of Zircaloy-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

The apparatus used in this study consists of a furnace containing an alumina furnace tube. 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 temperature range was from 800-1200 °C.

3. Results

Fig. 1 and 2 show the result of measuring the weight gain in each temperature under the air and steam at 1atm. Red line shows the result of oxidizing normal claddings and blue line dissolved hydrogen claddings, respectively. It was confirmed that under all the temperatures in air condition, weight gain of dissolved hydrogen claddings was increased by app. 20-50%. However, in steam condition, weight gain represented different result. In other temperature, weight gain was confirmed to be increased by app.25-40% like the case of air condition but at 1200C, weight gain increase of app. 5% was confirmed. In view of this result, it could be realized that hydrogen effect was confirmed in all the oxidation excepting oxidation at 1200C in steam condition.

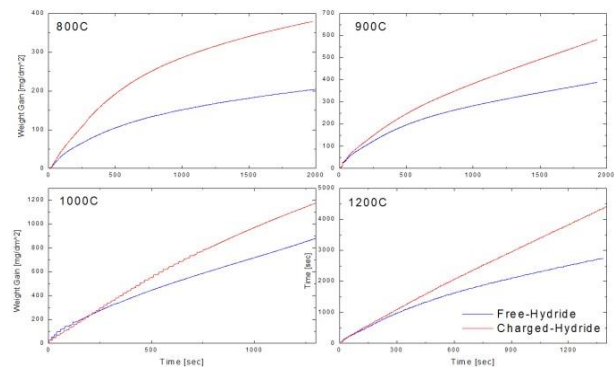


Figure 1. Weight gain of the air oxidation in hydrogen dissolved and hydrogen free (normal) Zry-4 specimens

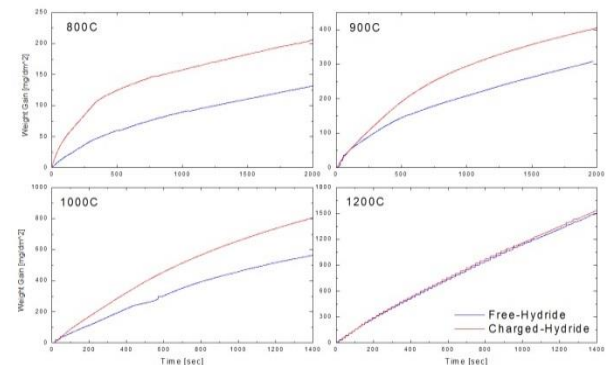


Figure 2. Weight gain of the steam oxidation in hydrogen dissolved and hydrogen free (normal) Zry-4 specimens

When observing optical micrographs of air oxidation in Fig.3, while most of metal layer of dissolved hydrogen claddings were disappeared and oxidized, relatively much portion of metal layer of normal claddings remained. However, it could be confirmed that in these two claddings, heavy local oxidation was taken place commonly and ZrN was mainly generated between metal layer and oxide layer of this local oxidation. As generation of ZrN is increased, penetration is taken place around this area and it led to increase of oxidation increase again.

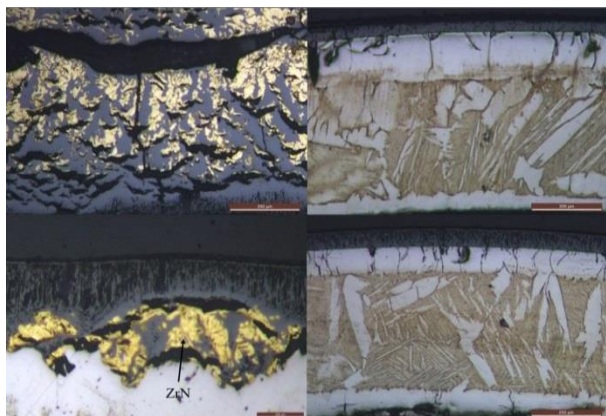


Figure 3. Optical micrographs of the hydrogen dissolved (up) and normal (down) Zry-4 specimen after air (left) and steam (right) oxidation at 1200C

Fig.4 shows SEM micrographs of the hydrogen dissolved Zry-4 specimen after the air oxidation at 1200C. In this image, more hydride was observed around local oxidation penetration compared with other oxide layer. The hydrogen could be exert its influence on ZrN formation. Therefore, it is showed that as this hydrogen affected the formation of ZrN, weight gain is taken place resultantly.

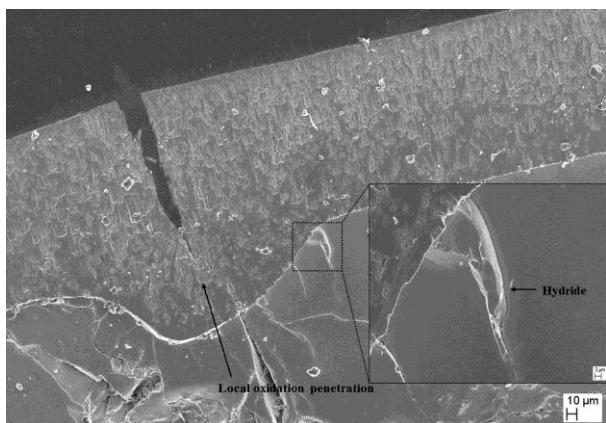


Figure 4. SEM micrographs of the hydrogen dissolved Zry-4 specimen after the air oxidation at 1200C

Fig. 5 shows raman spectrum depending on depth of the part where ZrN is formed. It could be confirmed that in each depth, height of ZrN peak is different. In other words, by this peak, an area where relative fraction of ZrN is high could be identified.

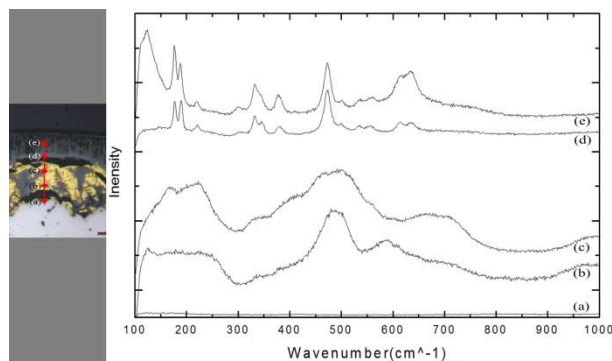


Figure 5. Raman spectrum of the normal hydrogen Zry-4 specimen after the air oxidation at 1200C

4. Discussion and Conclusions

The oxidation process is taken place by chemical reaction to the direction where Gibbs free energy is low at each temperature. As Gibbs energy of ZrO_2 is lower than ZrN, most of zirconium is reacted with oxygen. However, as shown on Fig. 3, ZrN is generated between oxide layer and metal layer. In other words, at the sub-stoichiometric oxide, ZrO_xN_y is considered to be generated as a result of zirconium being reacted together with oxygen and nitrogen and then ZrN is generated additionally. As ZrN is generated in this process, penetration is formed and as the oxidation rate is accelerated more abruptly, weight gain is taken place rapidly. In the meanwhile, this rapid increase oxidation rate is more generated in dissolved hydrogen claddings. In addition, it could be confirmed that hydride exists in local oxidation of Fig. 5. In other words, hydrogen is considered to affect formation of ZrN.

Cristal growth mechanism is generated depending on free energy change. In other words, when total free energy change exceeds critical free energy, it is generated as embryo. Radius of the nucleus being generated at this time is critical radius. It is believed that this critical radius is affected by hydrogen. In view of solubility of each temperature under this study, dissolved hydrogen is to be completely dissolved in metal. It is considered that as this completely dissolved hydrogen affects variation in free energy of zirconium oxidation, critical radius is reduced and growth of ZrN is enhanced. Finally, a favorable condition where ZrN could grow is provided. Therefore, a study on how this hydrogen affects free energy is required to be further performed in the future.

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