

## A Study on the Reaction Kinetics of Zircaloy-4 with H<sub>2</sub>/H<sub>2</sub>O Mixture

JI MIN LEE, JU SEONG KIM, YONG SOO KIM\*

Department of Nuclear Engineering, Hanyang University,  
17 Haengdang-Dong, Sungdong-Ku, Seoul 133-791, South Korea

\*Corresponding author : yongskim@hanyang.ac.kr

### 1. Introduction

Through-wall defects resulting from debris fretting, grid to rod fretting, and PCI can develop in the fuel rod during reactor operation. In this case, coolant water enters inside fuel rod through the defect hole. Then it flashes into steam in the gap and the steam causes not only oxidation of inner surface of cladding but also generation of hydrogen takes place in the gap continuously as the cladding corrosion reaction. Thus, the gap is filled with hydrogen/steam mixture. It is well-known that the hydrogen/steam pressure ratio,  $P(\text{H}_2)/P(\text{H}_2\text{O})$ , is higher than certain critical value,  $\beta_{\text{cr}}$ , the oxide no longer plays a protective role and massive hydriding occurs[1]. This phenomenon is called the secondary hydriding degradation.

The critical ratios are known to be order of  $10^2$ - $10^6$  for zirconium alloy depending on specimen geometry, temperature, and total pressure[1-5]. Few studies, however, on the critical value have been reported in case of Zircaloy-4 which is widely used for PWR fuel cladding. In addition, clear understanding of secondary hydriding mechanism has not been established yet so far[6].

In this study, thorough experimental investigations were carried out in order to determine the critical value for commercial Zircaloy-4 and give a mechanistic understanding of the secondary hydriding degradation.

#### 2.1 Specimens

All specimens were cut out with 10 mm in length from the commercial Zircaloy-4 cladding tubes for test. Then they were pickled in a solution of 3% HF, 47% HNO<sub>3</sub> and 50% H<sub>2</sub>O. Finally, they were cleaned in an ultrasonic bath of mixed solution of acetone and ethyl alcohol for 10 minutes.

#### 2.2 Test conduct

Experiments were carried out under atmospheric pressure using TGA whose schematic diagram is shown in Fig.1. Specimen was freely hung from a Pt wire connected to microbalance weighing cell whose sensitivity is 0.1  $\mu\text{g}$  (S3D-P, Satorius). Reaction chamber was vacuumized by the rotary pump to about  $10^{-3}$  Torr and ultra-high purity(99.9999%) He gas entered the chamber until it has reached atmospheric pressure. Then the chamber is maintained at 1 atm during He gas flowing in and out of the chamber at flow

rates of 40 cc/min. For isothermal tests, reaction chamber was heated to the desired temperature with flowing the He gas and thermally equilibrated for 10 minutes.

Then, H<sub>2</sub>(99.999%) gas intentionally flowed through the chiller filled with crushed ice or water to make desired hydrogen/steam mixture. Then the mixture gas flowed into the reaction chamber at the flow rate of 120 cc/min and total pressure of 1 atm. The weight gain was measured by an in-situ method and the data was acquired by a data acquisition system connected to a personal computer.

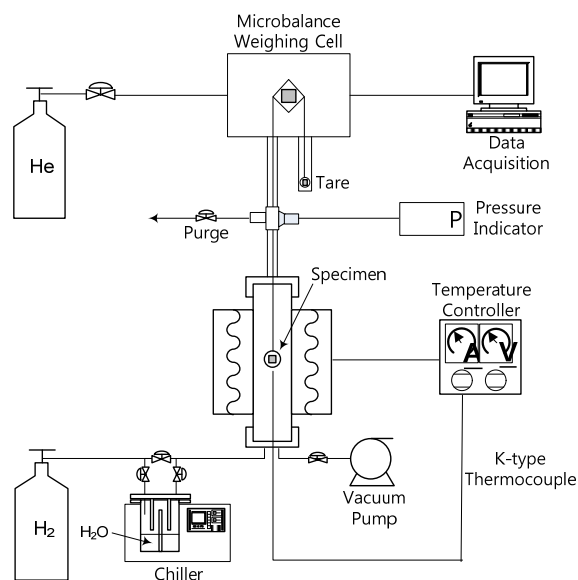


Fig.1. Schematic diagram of TGA.

### 3. Results and Discussion

Reaction results with H<sub>2</sub>/H<sub>2</sub>O mixture at several temperatures are shown in Fig. 1 and their corresponding numbers are presented in Table 1.

As seen in the figure, reaction can be divided into three stages. At the beginning of the stage, weight gain increases linearly due to direct reaction of bare cladding surface with gaseous hydrogen. After that, oxides which play a protective role for hydrogen permeation are formed and oxidation which is diffusion controlled process becomes a dominant reaction combined with slow hydriding distinct from the commonly-observed 'pickup'. Finally, a transition to linear kinetics occurs at

certain specific weight gain as well as weight gain increases rapidly, linearly with reaction time. It is believed that the Zircaloy-4 undergoes massive hydriding because it is well-known that massive hydriding kinetics of zirconium alloys follow a linear late law[7].

Meaning of mentioned above is that onset of massive hydriding does not occur immediately, although  $P(H_2)/P(H_2O)$  is higher than critical value. It means that there is a required time to transition to initiate the massive hydriding. That is, when oxide film reaches a certain thickness regardless of temperature, mechanical defects such as vertical crack are made and these act as shortcuts for direct permeation of hydrogen through the bare surface. It seems that the initiation of secondary hydriding depends on whether breakaway, loss of integrity, of oxide occurs or not, rather than value of  $P(H_2)/P(H_2O)$ . This will be demonstrated by the microstructural analysis.

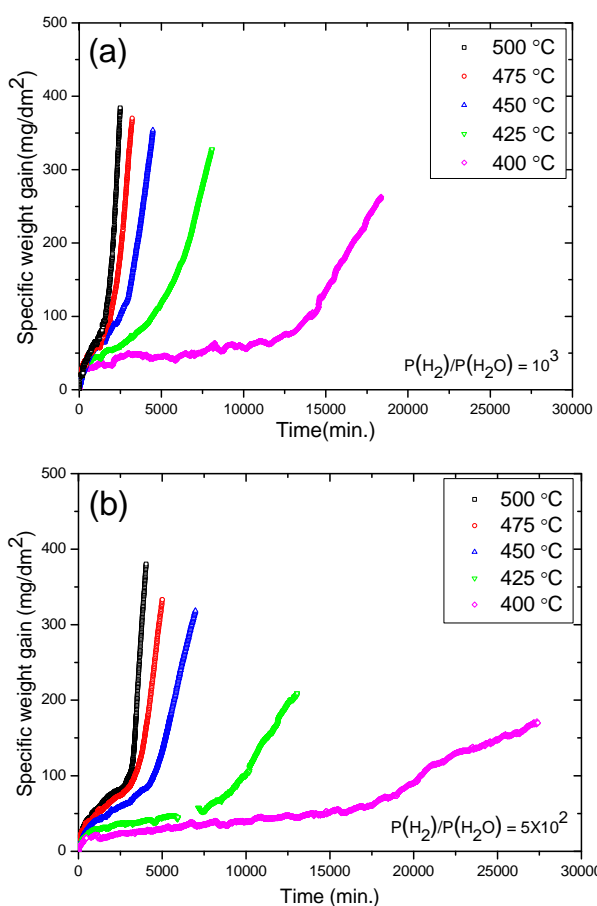


Fig.2. Specific weight gain of Zircaloy-4 tube segment with  $H_2/H_2O$  mixture at several temperatures,  $P(H_2)/P(H_2O)$  is (a)  $10^3$  and (b)  $5 \times 10^2$ .

Meanwhile, it can be seen in Table 1 that lower value of  $P(H_2)/P(H_2O)$  increases the transition time at same temperature. This is because the higher steam concentration makes the oxide continuously maintaining its protectiveness against hydrogen permeation.

In addition, the transition time in this out-of-pile tests is a maximum value to initiate secondary hydriding degradation. Because there is radiation damages induced by fission fragments and neutrons under in-pile condition so that intense generation of defects in the oxide film can causes acceleration of breakaway phenomenon and hydrogen can permeate easily through the oxide film.

Table 1. Results of the experiments at total pressure of 1 atm.

| Test | $\beta$         | Temp. (°C) | Time to transition (min) | Hydriding rate (mg/dm <sup>2</sup> /min) |
|------|-----------------|------------|--------------------------|--|
| ZA1  | $10^3$          | 500        | 1578                     | 0.284-0.389                              |
| ZA2  | $10^3$          | 475        | 1860                     | 0.263                                    |
| ZA3  | $10^3$          | 450        | 2194                     | 0.124-0.164                              |
| ZA4  | $10^3$          | 425        | 4320                     | 0.089                                    |
| ZA5  | $10^3$          | 400        | 13120                    | 0.024-0.038                              |
| ZB1  | $5 \times 10^2$ | 500        | 2703                     | 0.335                                    |
| ZB2  | $5 \times 10^2$ | 475        | 2990                     | 0.180                                    |
| ZB3  | $5 \times 10^2$ | 450        | 3978                     | 0.095                                    |
| ZB4  | $5 \times 10^2$ | 425        | 8240                     | 0.035                                    |
| ZB5  | $5 \times 10^2$ | 400        | 18006                    | 0.009                                    |

#### 4. Conclusions

Based on the current experimental results, following conclusions are drawn:

- 1) The reaction can be divided into three stages. First, hydriding occurs due to direct reaction of bare surface with gaseous hydrogen. Second, oxides are formed and it plays a protective role for hydrogen permeation. Finally, a transition to massive hydriding occurs with linear rate law at certain specific weight gain.
- 2) When oxide film reaches a certain thickness regardless of temperature, mechanical defects are made and these act as shortcuts for direct permeation of hydrogen through the bare surface. It seems that the initiation of secondary hydriding depends on whether breakaway, loss of integrity, of oxide occurs or not, rather than value of  $P(H_2)/P(H_2O)$ .
- 3) Lower value of  $P(H_2)/P(H_2O)$  increases the transition time to initiate the massive hydriding at same temperature because the higher steam concentration makes the oxide continuously maintaining its protectiveness against hydrogen permeation.

It is insufficient data to elucidate the whole reaction kinetics and critical value. Therefore, experiments will be added and microstructural analysis will be used to fully understand the mechanism of secondary hydriding.

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