

A Study of Zircaloy Reaction with Steam/Hydrogen Mixture

JU SEONG KIM, JI MIN LEE, 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

Under in-reactor operating conditions, zirconium alloy fuel cladding can be exposed to through-wall breach (a primary defect) resulting from debris fretting, grid to rod fretting and PCI. In this case, coolant water enters the gap through the defect hole due to difference of the pressure of internal fuel rod and coolant. Then the coolant flashes into steam in the gap. The steam causes not only oxidation of inner surface of cladding but also hydrogen builds up continuously as a reaction product. At this moment, the gap is filled with a hydrogen/steam mixture.

If the hydrogen/steam ratio is higher than certain critical value, the oxide no longer plays a protective role for massive hydrogen permeation. The critical ratio for Zircaloy-2 is known to be order of 10^2 - 10^6 depending on temperature, pressure, surface condition, and oxide layer property (table 1) [1-5].

Thus in this study, several tests were carried out for commercial Zircaloy-4 in order to determine the critical value of the ratio of hydrogen to steam pressure causing the massive hydriding in the temperature range of 300-500 °C as a function of hydrogen/steam ratio from 10^3 to 10^7 under atmospheric pressure by in-situ measurements using TGA.

Table 1. Comparison of critical hydrogen-to-steam ratios for massive hydriding

Material	Temperature (°C)	Critical ratio	Reference
Zircaloy-2	343	10^{6-8}	[1]
Zircaloy-2	400	10^2	[2]
Zircaloy-2	320	10^3	[3]
Zircaloy-2	300, 400	$10^3, 10^2$	[4]
Crystal-bar Zr	400	10^3	[5]
Zircaloy-4	500	$\leq 10^3$	Present work

2. Experimental

2.1 Specimens

All specimens for hydriding testing were cut off from the commercial Zircaloy-4 cladding tubes. The segments were 10 mm in length and both ends of the specimens were ground carefully up to 2000-grit of SiC paper. Then all the segments were pickled in a solution of 3% HF, 47% HNO₃ and 50% H₂O for 2 minutes to

remove pre-filmed surface oxide and finally cleaned in an ultrasonic bath of acetone for 3 minutes.

2.2 Test conduct

Prepared specimens were freely hung from a Pt wire connected to TGA whose sensitivity is 1 µg (S3D-P, Satorius). Reaction chamber was vacuumized by the rotary pump to about 10^{-3} torr and ultra-high purity (99.9999%) helium gas entered the vacuumized chamber until the chamber has reached atmospheric pressure. Then, the helium gas flowing in and out of the chamber at flow rates of 300 cc/min continuously. For isothermal tests, the specimens were heated to the desired temperature at a rate of 15 °C/min in flowing inert helium gas and thermally equilibrated for 10 minutes. Then turned off the helium gas and hydrogen/steam mixture gas was directly injected into the reaction chamber at the flow rate of 200 cc/min. 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. The experiment is completed by sudden weight decrease caused by flaking-off of the embrittled specimen.

3. Results and Discussions

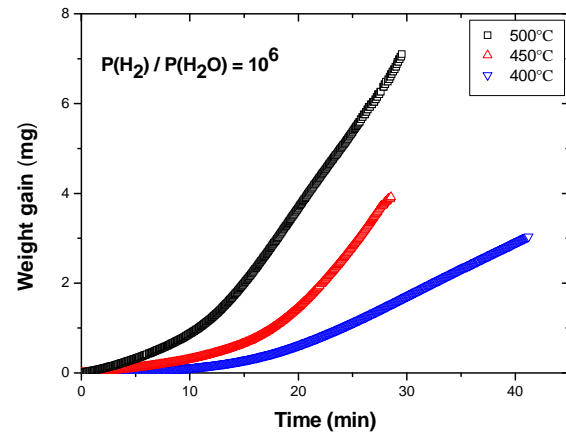


Fig. 1. Weight gain behaviors in the hydriding reaction of Zircaloy-4 at several temperatures at $P(H_2)/P(H_2O) = 10^6$

It has been reported that the hydriding reaction is surface-reaction controlled and hydriding kinetics follows a linear rate law. Therefore, weight gain rate can be expressed as follows:

$$\Delta W = kt \quad (1)$$

Where, ΔW is weight gain in mg/dm^2 , t is reaction time in minutes, and k is the reaction rate constant in $\text{mg}/\text{dm}^2/\text{min}$. The rate constant k consists of two terms, pre-exponential factor k_0 and activation energy Q as shown:

$$k = k_0 \exp(-Q/RT) \quad (2)$$

Where, R is the gas constant and T is absolute temperature in Kelvin.

Fig. 1 shows the weight gain behaviors in the hydriding reaction of Zircaloy-4 at $P(\text{H}_2)/P(\text{H}_2\text{O}) = 10^6$.

As seen in the figure, little weight gain by the hydrogen absorption is observed at the initial stage for a certain period of time, but after the incubation period, weight gain increases rapidly, almost linearly with reaction time. It was reported that the surface oxide film always forms during prior heating of the chamber even under a vacuum of 10^{-7} Torr[6,7], and thus, it is concluded that thin surface oxide film grown during the prior heating contributed to incubation time by acting as a protective film for hydrogen permeation.

On the other hands, steam/hydrogen mixture has different kinetic behaviors. Hydriding reaction rates are increase with Increasing $P(\text{H}_2)/P(\text{H}_2\text{O})$. Conversely, hydriding reaction rates decrease with decreasing $P(\text{H}_2)/P(\text{H}_2\text{O})$. However, compare the steam oxidation with the $P(\text{H}_2)/P(\text{H}_2\text{O}) = 10^3$, mixture gas reactions are relative faster than steam oxidation. So called, slow hydriding region exist in the reactions.

Fig. 2 shows the weight gain behaviors at 500°C in hydrogen/steam mixture gas. Rate of the hydrogen/steam mixture gas increases with increasing $P(\text{H}_2)/P(\text{H}_2\text{O})$ value. It is believed that there is some critical hydrogen/steam ratio to penetrating the oxide layer in range of the $P(\text{H}_2)/P(\text{H}_2\text{O})=0-10^3$.

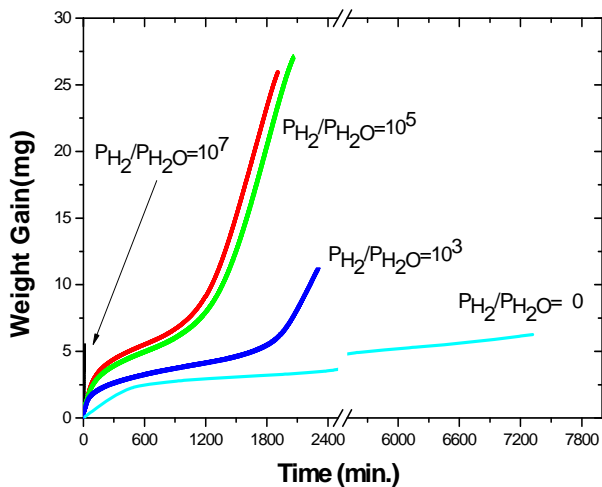


Fig.2. Weight gain behaviors in the hydriding reaction of Zircaloy-4 at 500°C with $P(\text{H}_2)/P(\text{H}_2\text{O}) = 0-10^7$

For hydrogen/steam partial pressure ratio from 10^3 to 10^7 , Zircaloy-4 reaction with steam/hydrogen mixture gas experiment has been conducted.

In mixture gas environment, at the beginning of the reactions, reaction rate are very fast and after the fast reaction, second stage are oxidation reaction combined with hydrogen reaction, that is slow hydriding. And finally, weight gain increases rapidly, almost linearly with reaction time. It is believed that reaction relate to hydrogen permeation.

However, it is still insufficient data to elucidate the whole reaction kinetics and critical hydrogen to steam ratio. Therefore, in order to find the critical ratio of steam/hydrogen mixture gas and reaction kinetics, experiment will be added in the temperature range of $300-450^\circ\text{C}$ as a function of hydrogen/steam ratio.

REFERENCES

- [1] R.F.Boyle, T.J.Kiesiel, "Hydrogen Permeation of Zircaloy-2 Corrosion Films", *WAPD-BT-10* (1958)
- [2] D.W. Shannon, *Corrsion* 19(1963) 414
- [3] R. L. Gibby, Hydriding of PRTR fuel rod end caps, BNWL-150, 1965
- [4] K. Une, "Kinetics of Reaction of Zirconium Alloy with Hydrogen" ,*Journal of Less-Common metal.* 57(1978) 93
- [5] Y.S.Kim et al, "High pressure hydriding of sponge-Zr in steam-hydrogen mixtures", *Journal of Nuclear Materials* 246(1997) 43-52
- [6] M.Blat, J.Bourgoin, "Corrosion Behavior of Zircaloy-4 cladding Material: Evaluation of the Hydriding Effect", *Proceedings of International Topical Meeting on Light Water Reactor Fuel Performance*, Portland, Oregon, 250 (March 2-6 1997)
- [7] G.E.Zima, "A Review of the Zircaloy-2 Hydriding Problem", *HW-665378* (1960)

4. Conclusions