Journal of the Korean Nuclear Society
Volume 30, Number 5, pp.396~402 October 1998

Pressure Effects on Zircaloy-4 Steamside Corrosion and Hydrogen Pick-up

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(Received August 25, 1997)

Abstract

Experiments on the steamside corrosion and hydrogen pick-up of Zircaloy-4 under high pressure up to 10.3MPa are carried out to estimate the pressure effects on the kinetics. Temperature and reaction time are determined to be 370°C and 72hours for the pre-transition test and 700°C and 210minutes for the post-transition test, respectively. Results show that under 10.3MPa pressure the oxidation reaction is 50% and 100% enhanced in the pre- and the post-transition regime, respectively. Total amount of hydrogen uptake in the reaction is proportionally increased as corrosion weight gain is elevated. However, pick-up fraction is not affected by the high pressure. The fraction is almost twice greater than that in the waterside corrosion. Edges in the specimens play a certain role in the enhancement, especially in the post-transition regime. To identify physical property changes of oxide film such as micro-cracks or micro-pores, careful and thorough examination must be needed with some special techniques.

1. Introduction

Hydriding of Zircaloy cladding has been one of the important causes of fuel failures in Light Water Reactors. Operating experiences of nuclear power plants show that past capacity factor losses due to fuel failures have been principally caused by hydriding of Zircaloy cladding (PWR, BWR, and PHWR) and by pellet cladding interaction (BWR) [1]. Internal hydriding of Zircaloy cladding would be a persistent cause of defects and occasional fuel failures in early LWRs [2,3]. Recently catastrophic fuel failures due to secondary internal hydriding were reported and have initiated a worldwide fuel-failure survey involving over thirty utilities and international co-research on the issue [4-6].

In the secondary hydriding, coolant enters inside fuel rod through a small through-wall defect and flashes into steam. The steam pressurizes inside the rod and reaches system pressure rapidly in hours or days and then the high pressure steam begins to oxidize the inner wall of the cladding. With prolonged oxidation, oxygen is depleted and hydrogen is built up continuously in the gap between fuel pellet and inner surface of the cladding. This situation may lead to a critical condition of hydrogen-rich steam starvation for accelerated or massive hydriding. At this moment the cladding may be subject to a localized accelerated hydriding and to the potential of massive hydriding failure if the oxide layer is no longer protective. In order to meet the demand of high reliable performance, this failure may be one of the critical problems of the nuclear fuel elements in coming years. In actual, hydrogen permeation or penetration through the oxide is one of the crucial issues in the hydriding failures, either primary or secondary. With increasing oxide thickness 'incubation' time lengthens before the onset of the hydriding reaction. The breakdown process of the surface oxide film depends on the nature of the oxide layer such as self-applied stress and stoichiometry change and/or environments such as high pressure and H_2/H_2O ratio and so on.

However, few experimental data on the high pressure steam corrosion and hydrogen pick-up of zirconium alloys at low temperature are available although they are essential to form the scientific basis for the elucidation of the accelerated or massive hydriding mechanism. Thus, in this paper, steam corrosion and hydrogen pick-up of Zircaloy-4 under high pressure up to 10.3MPa are experimentally examined to provide one of the fundamentals to the understanding of the defected PWR fuel behavior.

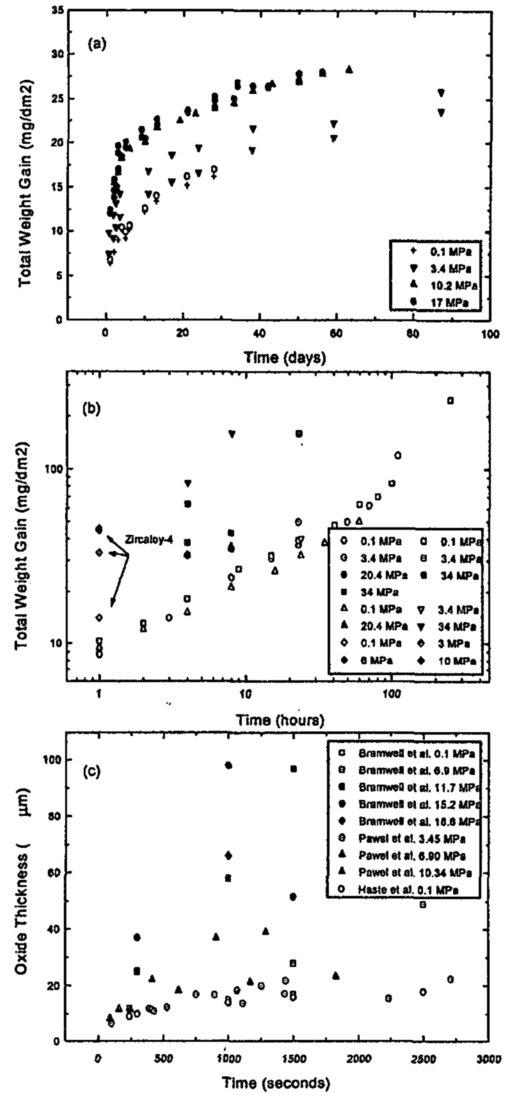

Fig. 1. (a) Effect of Pressure on Zircaloy-2 Oxidation in 350℃ Steam [8], (b) Oxidation of Zircaloy-2 in 500℃ Steam [8], and (c) Oxide Thickness of Zircaloy-4 at Various Steam Pressure at 900℃ [7, 9]

2. Review of Earlier Works

Two mechanisms are available, in general, to explain how zirconium oxide film permits hydrogen penetration. In one mechanism, mechanical defects such as micro-cracks, micro-pores, inter-metallic particle sites, as well as subgrain boundaries and dislocation networks, are believed to provide hydrogen atoms with shortcut paths to zirconium substrate. In the other, the penetration is ascribed to the presence of substoichiometry in the oxide whose abundant oxygen vacancies permit more rapid movement.

In fact, several authors have claimed that micro-pores or micro-cracks may develop more rapidly in the oxide film grown in the high pressure corrosion than in the 0.1MPa pressure oxidation and these micro-defects lead to the enhancement of oxidation rate and possibly to a massive hydriding of zirconium alloy base metal [7-9]. Pawel observed the pressure effect at 905℃ in the range of 3.4MPa ~ 10.3MPa while no effect observed at 1100℃. He explained that the cause of the enhancement is due to micro-cracks quickly developed inside oxide layer during the high pressure reaction and at relatively high temperature above 1100℃ rapid self-healing of the cracks with time produces no effects [7]. Cox claimed that he also observed the enhancement under 34MPa steam corrosion of Zircaloy-2 at temperature of 350℃ ~600℃ and the enhancement is caused by increasing micro-pores in the oxide [8]. The enhancement was also measured by Bramwell in 18.6MPa steam reaction at temperatures of 800~900℃ [9]. In order to provide readers with comprehensive explanation on this issue at the broader temperature range the experimental results of the previous researchers are collectively plotted in Figure 1.

Recently it was revealed that the accelerated or massive hydriding takes place more easily with lower critical hydrogen-to-steam ratio under high pressure than that does under 0.1MPa pressure [10].

3. Experiments

Experiments are carried out with the twin autoclave system in Figure 2. It is designed and manufactured to allow to study the corrosion reaction as independent functions of pressure and temperature. Its maximum design temperature at 15MPa is 625℃. Details can be referred to reference [11].

All the experimental variable sets, pressure, temperature, and reaction time, are chosen to avoid corrosion nodule formation which can take place in the steam corrosion of zirconium alloys. In order to obtain data reproducibility a batch of three or four specimens is loaded in each experiment.

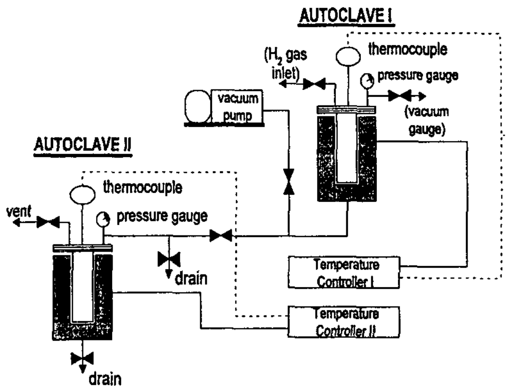

Fig. 2. High Pressure/High Temperature Twin Autoclave System

Since it is known that specimen edges play significant role in the hydriding zirconium alloy the influence of edges is examined, simultaneously with the corrosion tests, as a function of surface-to-edge ratio with various lengths of tubes from 3mm to 100mm. After each experiment thorough micro-graphic examinations are followed.

Specimens are short tubes cut out of Zircaloy-4 tubes from SANDVIK and pickled in the solution (50% H_2O+47%HNO_3+3%HF) for three minutes before loading. Their weights are measured before and after the tests with electro-micro-balance whose sensitivity limit is 10^{-5}g. Hydrogen content is analyzed with the hydrogen determinator (RH-404) from LECO Corp.

4. Results and Discussion

First, to see the pressure effects on the oxidation in the pre-transition regime, test temperature and reaction time are determined to be 370℃ and 72hours, respectively, and the total weight gain and hydrogen pick-up are examined. Figure 3a) shows that total weight gains under 10.3MPa

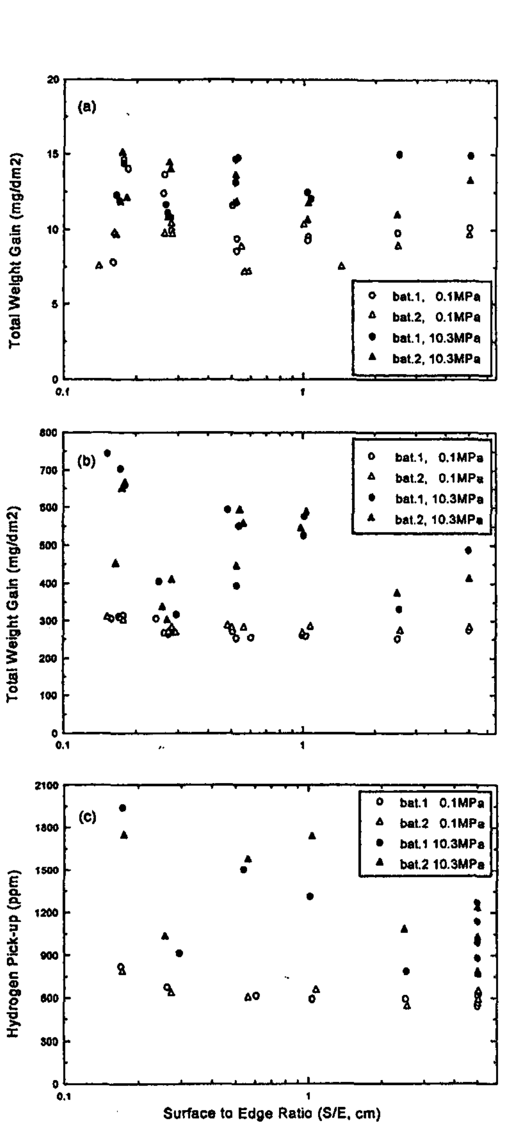

Fig. 3. Total Weight Gain and Hydrogen Pick-up of Zircaloy-4 Tube As a Function of Edge Fraction (a) 370℃, 72hrs, (b) 700℃, 210min, and (c) 700℃, 210min

steam pressure are enhanced about 50% compared to that under 0.1MPa steam. Since hydrogen pick-up is believed to depend on specimen geometry principally due to the presence of edges and corners on the surface it is investigated as a function of surface-to-edge ration ranging from 0.17 to 5.0cm at the two pressures. Both total weight gain and hydrogen pick-up are insensitive to the extent of the edge fraction.

For the test in the post-transition similar experiments at 700℃ under the two pressures, 0.1MPa and 10.3MPa, are carried out for 210minutes. Figure 3b) reveals that total weight gains are about 100% greater under 10.3MPa steam environment and tend to increase with increasing edge fraction. The low enhancement at S/E=0.3 in the figure seems to be due to the limitation of ex-situ experiments, i.e., before and after measurements. The content of hydrogen picked up by the alloy in the reaction is plotted in Figure 3c), which shows that hydrogen uptake is increased as much as the total weight gain is enhanced and the edge effect on the pick-up is very similar to that on the total weight gain elevation. This is partly supporting the finding in reference [10] that high pressure oxidation and hydriding of Zircaloy requires lower critical ratio of H_2/H_2O than 0.1MPa pressure oxidation.

These results are in good agreement with earlier works [7-9]. In fact, most of collected experimental data are demonstrating that significant enhancements are observed at around 600℃ while at relatively low temperature around 300℃ the effect is insignificant because the kinetics is too slow and it disappears when temperature exceeds 1100℃ because micro-cracks or micro-pores developed during high pressure reaction are annealed out at high temperature. Practically it implies that during reactor operation high pressure steam oxidizes the inner-surface of the cladding more rapidly than expected after steam ingression in a defective fuel rod and hydrogen atoms produced during the corrosion reaction are picked up as much as the oxidation kinetics is enhanced.

In order to examine the onset of the pressure effects on Zircaloy corrosion reaction total weight gain measurements are carried out as a function of

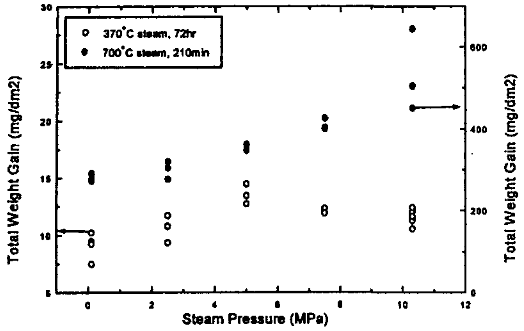

Fig. 4. Total Weight Gain Changes with Increasing Steam Pressure

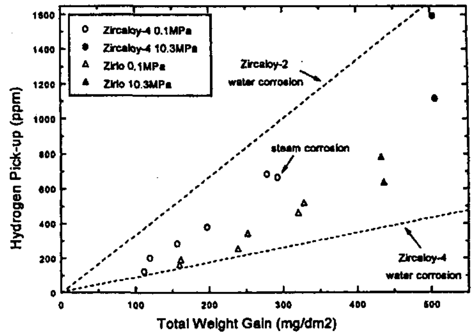

Fig. 6. Hydrogen Pick-up Fraction and Total Weight Gain (700℃)

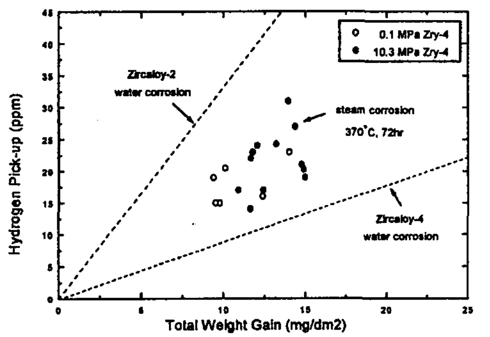

Fig. 5. Hydrogen Pick-up Fraction and Total Weight Gain

steam pressure (Figure 4). The figure shows that as the steam pressure increases the degree of the enhancement continuously escalates without a certain threshold within the pre-transition regime, on the other hand, past the pre-transition regime it rather saturates early when the pressure reaches about 5MPa.

It is well-known that in the waterside corrosion of zirconium alloys there is a certain relationship between hydrogen pick-up and total weight gain and the fraction of the pick-up is 10~15% for Zircaloy-4 whereas it is about 40~55% for Zircaloy-2 [12,13]. In this study the fraction in the steam corrosion is evaluated and plotted for the comparison with that in the waterside corrosion. Figure 5 shows the pick-ups in the pre-transition regime while Figure 6 shows the pick-ups in the post-transition regime. The fraction is almost twice larger than that in the waterside corrosion, as shown in the figures, and not affected by high pressures. Only the total amount of hydrogen uptake by the alloy increases as much as the total weight gain is enhanced.

As mentioned in the previous section, high pressure effects on the Zircaloy oxidation appear to be associated with some physical or chemical changes in the oxide film rather than simply a thermodynamic influence. Thus, micro-graphic examinations are conducted after each experiment using optical microscopy and scanning electron microscopy to detect any micro-cracks or micro-pores. Figure 7a) and 7b) show the oxide films of Zircaloy-4 tube grown under 0.1MPa and 10.3 MPa pressure, respectively. The former has many small lateral cracks while radial cracks with small lateral cracks are observed in the latter. However, these cannot be micro-cracks developed in the course of physical property changes but the cracks due to the specimen geometry. As expected, it is not easy to identify such property changes in the films, thus, thorough examination should follow with some special techniques in the following investigation.

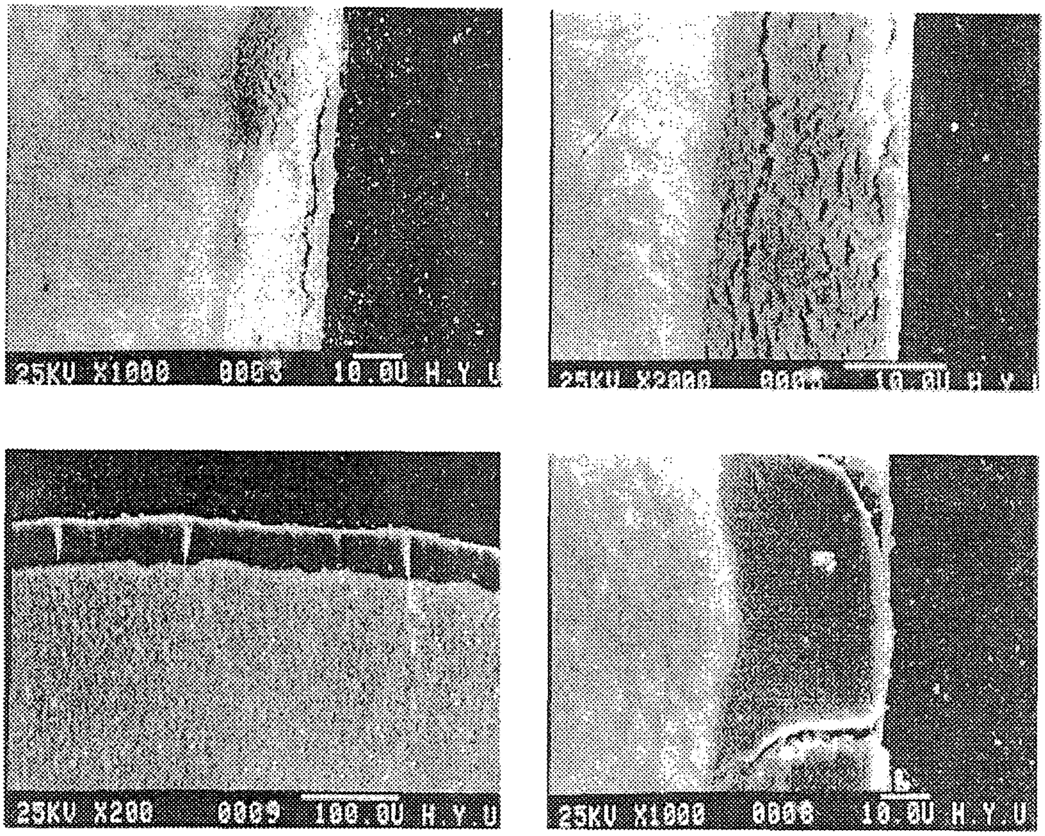

Fig. 7. Micrograph of Oxide in Zircaloy-4 Tube (a: top figures) 0.1MPa Steam at 700℃, 210min (b: bottom figures) 10.3MPa Steam at 700℃, 210min

5. Conclusions

Under 10.3MPa the kinetics of steam oxidation of Zircaloy-4 tube at 370℃ is about 50% enhanced in the pre-transition regime compared to that under 0.1MPa steam corrosion whereas it increases 100% at 700℃ in the post-transition regime. In both cases the total amount of hydrogen uptake by the Zircaloy base metal increases as much as the total weight gain enhanced. However, pick-up fraction is not affected by the high pressure and almost twice greater than that in the waterside corrosion.

Edge effect on the total weight gains and the hydrogen uptake is noticeable in the high pressure corrosion, especially in the post-transition regime.

There seems to be no onset or threshold steam pressure for the high pressure effect on Zircaloy-4 oxidation. The enhancement becomes saturated early around 5MPa in the pre-transition while it is continuously increasing with increasing pressure in the post-transition.

Careful and thorough examination of the characteristics of oxide film grown under high pressure, i.e., micro-cracks or micro-pores, must follow with special techniques to study their effects further.

Acknowledgment

This work was supported by GRANT No. KOSEF 951-1001-060-2 from the Korea Science and Engineering Foundation.

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