Measurement of hydriding susceptibility of Zircaloy cladding by the tube-burst technique at high pressure and high temperature

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Abstract

High-pressure hydriding of Zircaloy (Zry) cladding was studied using the tube-burst technique. The aim was to demonstrate a practical laboratory test that reliably predicts the hydriding resistance of cladding. The test consists of pressurizing a section of tubing with hydrogen (wet or dry) and measuring the time to failure. Surviving specimens lasted 140 h, the maximum test time. Duplicate experiments were conducted in the temperature range 300–385°C to investigate the temperature dependence of hydriding as well as reproducibility. In addition, the effects of water vapor content in hydrogen gas and cladding surface condition on the hydriding susceptibility were investigated. The failure time was found to be highly sensitive to temperature. In dry hydrogen and for the particular type of cladding studied, a failure threshold of ≈ 340°C was observed. Above this temperature the failure time decreased rapidly with increasing temperature. Water vapor in the gas prevented hydriding for H_2/H_2O ratios less than 5.0×10^4. Chemical etching rendered the specimen immune from hydriding in the conditions of the test. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In a failed BWR fuel element, oxidation of the cladding inner surface by steam produces hydrogen in the fuel-cladding gap. Hydrogen formation may be enhanced by fission fragment recoil from the fuel into the gap, where water is decomposed into hydrogen and oxygen [1]. Hydrogen eventually penetrates the oxide scale on the cladding inner surface and forms zirconium hydride in the metal. This process can cause secondary cladding failure, manifest by axial splitting due to stress in the hydrided metal or by hydride blisters that pop off and expose fuel to the coolant [2–4].

The 'tube-burst' test is a recently developed laboratory technique designed to measure the resistance of Zircaloy (Zry) cladding to internal attack by hydrogen.

The method involves a tube-type specimen and nearly equal high pressures inside (H_2) and outside (He) the tube so that the pressure conditions of a failed fuel rod during reactor operation are closely simulated. This method avoids the edge effect that causes difficulties in the thermogravimetric test method [5–9]. The tube-burst method permits testing at realistic pressures (70 bar), thereby avoiding the atypical atmospheric or sub-atmospheric pressures used in the previous laboratory experiments [10–12].

The tube-burst technique was previously described as a simple laboratory test providing multiple measures of a particular cladding material's ability to resist secondary hydriding [13]. However, the reproducibility of the method was investigated in only a limited number of experiments. In addition, surface modifications during fabrication and by steam oxidation during the post-primary defect period were not investigated in [13].

The objective of the present study is to develop the tube-burst method as a simple laboratory test that reliably predicts cladding resistance to internal hydriding under defective fuel rod conditions in a BWR. The

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effects of temperature, water vapor content and initial surface treatment are investigated. Because of the stochastic nature of metal hydriding, characterizing the reproducibility of the results is a prime goal.

2. Experimental

Conventional Zry-2 cladding was used in the present study. The cladding has an ≈ 75 µm thick Zr–0.15 wt% Fe alloy liner on the inner surface. The chemical composition of the specimens is shown in Table 1. Most experiments were conducted using as-received tubing (cold-rolled structure). To determine whether surface condition was an important variable, some specimens were etched in a solution of 50 vol.% H_2O + 45 vol.% HNO_3 + 5 vol.% HF for 2 min prior to testing.

The experimental setup for the tube-burst test (Fig. 1) consists of a 30 cm long specimen (ID = 0.97 cm), a reaction chamber, two pressure transducers and a water supply. To eliminate the effect of edges and corners on hydrogen uptake, only a small center portion (2.5 cm long) of the specimen is heated to the desired temperature. The test was terminated when the specimen failed, as indicated by a sudden equalization of the inner and outer pressures. If no failure occurred, the test was terminated after 100–140 h.

The hydriding experiments were conducted either in a stagnant gas system or in a flowing gas system. In a stagnant gas system, the inside of the tube and the outer chamber were pressurized first with pure helium by opening the valves V1, V2 and V5 in Fig. 1 and by closing valve V7. After pressurizing, the system was sealed by closing the valves V1 and V2. The center portion of the Zry tube was heated to the desired temperature, and the leak rate of the specimen under these conditions was recorded for more than 20 h. If no leak was found, the helium gas inside the specimen was purged by opening V7 and replaced with hydrogen at 70 bar by opening V6 and closing V7. The hydrogen endurance test was started by closing V6, which isolates the specimen from its gas supply. The fixed amount of available hydrogen (6.2×10^{-2} mol) exceeds that required to completely convert the 2.5-cm long hot section to $ZrH_{1.63}$ (3.5×10^{-2} mol).
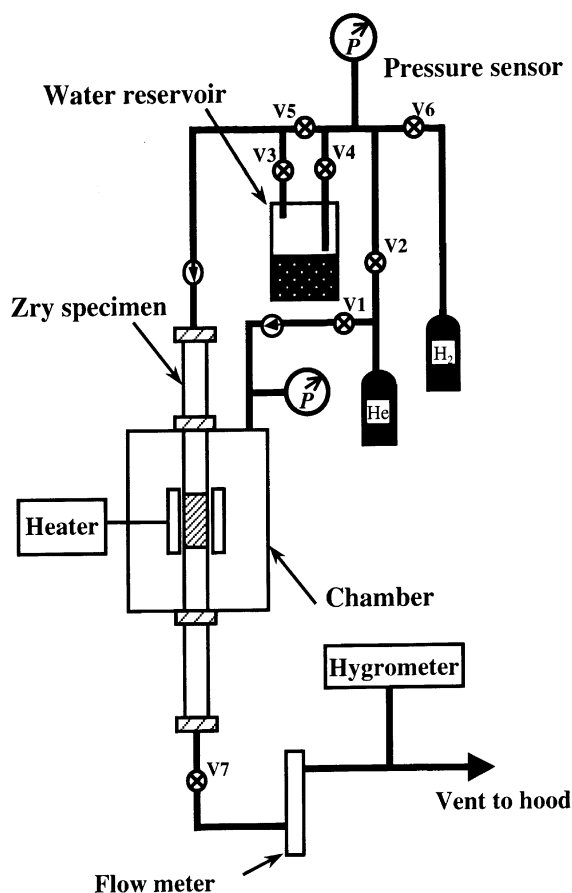

Fig. 1. Schematic diagram of apparatus for the tube-burst test.

Commercial grade hydrogen and helium gases were used in the present study. The most significant impurity in the hydrogen is water vapor because it controls the oxidant-to-hydrogen ratio. The water-to-hydrogen ratio could not be controlled in the stagnant-gas experiments, a deficiency that was remedied by the flowing-gas mode described below. With stagnant gas, little decrease in the inside hydrogen pressure was observed during an incubation time. After this period, the inside pressure decreased rapidly due to hydrogen absorption. The incubation time is defined as the time corresponding to the intersection of the extrapolated initial and final linear portions of the inside pressure curve [13].

Neither the incubation time nor the subsequent hydrogen absorption rate can be obtained in a flowing gas system. For this variant of the method, only the failure time was used instead to identify the hydriding property of the specimen. Hydrogen inside the tube was pressure-regulated to 70 bar with a flow rate of ≈ 0.4 l/min by opening the valves V3, V4 and V7, and closing valve V5. The outer chamber was pressurized with helium by opening valve V1. For 'dry' gas, the hydrogen flow

Table 1
Chemical composition of the cladding specimens

Elements	Concentration (wt%)
Sn	1.32–1.36
Fe	0.17–0.19
Cr	0.10–0.11
Ni	0.06–0.07
Fe + Cr + Ni	0.33–0.36
O	0.11–0.12
Zr	Bal.

through the tube specimen was controlled by closing the valves V3 and V4 and opening valve V5 in Fig. 1. The water content of the H_2 produced in this way was about 20 ppmv, as measured by the hygrometer at the outlet of the reaction vessel. With these valve settings reversed, the H_2 flowed into the room-temperature reservoir containing cloth saturated with water. This procedure produced about 120 ppmv of water in the hydrogen stream. In some tests, the gas was first dry, then partially saturated with water by passing through the water reservoir.

3. Results and discussion

3.1. Reproducibility

Typical plots of pressure vs. time for a failed specimen and one that survived in the present study are shown in Figs. 2(a) and (b), respectively. Fig. 2(a) shows that the inside hydrogen pressure, initially higher than the outside helium pressure, decreased slowly (due to leakage) up to the incubation time. Thereafter, the pressure decreased rapidly due to hydrogen absorption by the metal. When the tube failed, the pressure inside the tube instantaneously increased to the chamber pressure. Fig. 2(b) shows the pressure traces for a specimen that survived for the maximum time allotted for the test. Post-test examination revealed that the heated center portion of the specimen had not hydrided.

The conditions and outcomes for the hydriding test are summarized in Table 2. None of the specimens tested at 300°C, 320°C and 330°C failed. The results of the tests without a water reservoir at 340°C, 375°C and 385°C are shown in Fig. 3. The bars in these plots represent the observed failure times of individual duplicate tests. The solid points connected by the curve give the cumulate average failure time up to and including the current result. Thus, after n identical tests, the average time to failure is
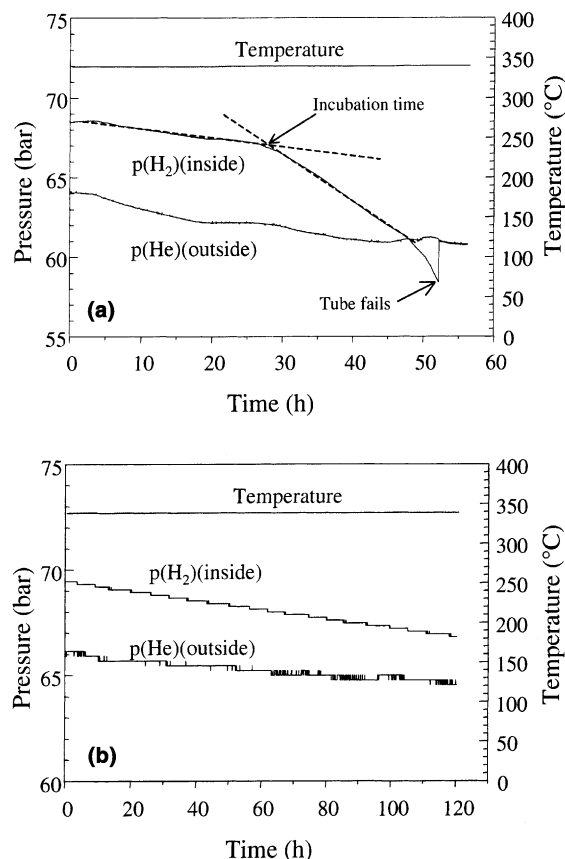

Fig. 2. Typical pressure vs. time curves using the stagnant gas method for: (a) a failed specimen; (b) an intact specimen.

$$\bar{t}_F = \frac{1}{n} \sum_1^n t_{Fi}. \tag{1}$$

This method of data analysis was adopted to smooth out the inherent variability of the individual failure times (t_{Fi}

Table 2
Summary of the hydriding tests using the tube-burst method

Temperature (°C)	Surface condition	Gas supply	Water reservoir	Water vapor (ppmv)	No. of specimens (survived/failed)
300	As-received	Stagnant gas	Bypassed	–	1/0
320	As-received	Stagnant gas	Bypassed	–	3/0
330	As-received	Flowing gas	Bypassed	20	1/0
	As-received	Stagnant gas	Bypassed	–	4/5
340		Flowing gas	Bypassed	20	1/0
	Etched[a]	Stagnant gas	Bypassed	–	3/0
375	As-received	Stagnant gas	Bypassed	–	0/4
			Bypassed	20	0/4
385	As-received	Flowing gas		80[b]	1/0
			Connected	120	1/0

[a] Specimens etched prior to testing as described in the text.
[b] Industrial grade hydrogen gas containing water vapor as an impurity.
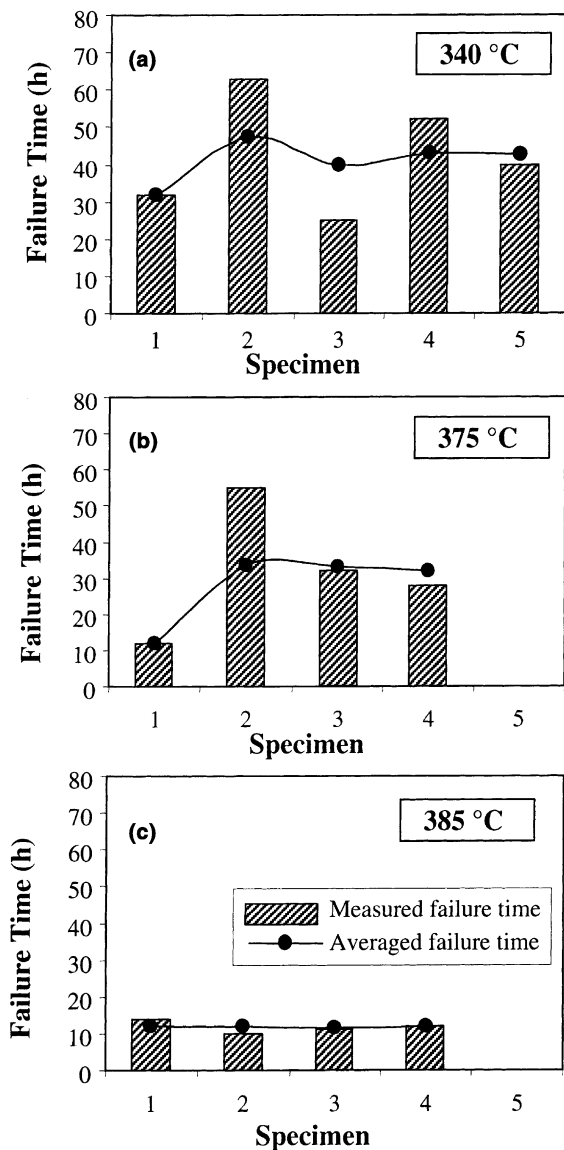
Fig. 3. Variation of the hydriding susceptibility in 20 ppmv H$_2$O with temperature; the points represent the average failure time up to and including the associated specimen number in the abscissa: (a) 340°C; (b) 375°C; (c) 385°C.

in Eq. (1)). A total of 10 specimens in the as-received state were tested at 340°C. This total included 9 using the stagnant gas method and one in flowing dry H$_2$. Five specimens survived while the rest failed in less than 63 h. The shortest failure time was 25 h and the average was about 40 h as indicated by the final solid circle in Fig. 3(a). At 375°C, four specimens were tested and all failed. The failure time was in the range 12–55 h and the average was about 30 h. At 385°C, all four specimens tested in dry H$_2$ failed after about 11 h.

Fig. 4 shows the change of the failure time with temperature in the range 300–385°C. The tests were done using as-received specimens in either the stagnant or flowing gas modes. By using the reciprocal of the failure times as the ordinate, the results for the survived specimens could be included by assuming $t_F = \infty$. The members of this group probably would have failed in finite times, but the maximum value of t_F^{-1} would have been <0.01. As seen in the graph, the failure time is highly temperature-dependent and is characterized by: non-detectable hydriding reaction at low temperature; for dry H$_2$, initiation of reactivity at a transition temperature; and rapid attack at higher temperatures. As shown in Fig. 4, the transition from non-reactive to reactive occurs over a fairly narrow temperature range around 340°C. The transition temperature in dry H$_2$ is a characteristic measure of hydriding resistance for the particular metallurgical condition of the specimen with the treatment (if any) of the surface.

The reason that half of the specimen tested in dry H$_2$ at 340°C survived and the other half failed (see Table 2) is probably due to the very narrow transition temperature range at 340°C. As test temperatures approach the transition temperature from below, the ratio of survivals to failures decreases.

The hydriding vs. temperature curves obtained from the previous study [13] for different cladding types showed shapes similar to those of the present specimens, but with transition temperatures of 30–40°C lower than that of the present experiment. The reason for this difference may be due to different liner Fe contents, and thermomechanical treatment during fabrication.

The dry-H$_2$ tests at 385°C were carried out in the flowing gas mode. The water vapor content was monitored throughout the experiment; it stabilized at 20 ppmv within 2 h, following which time the tests were performed. However, the experiments at 340°C and
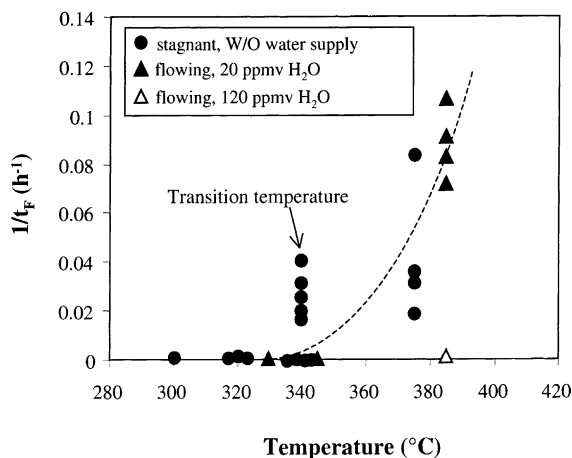

Fig. 4. Variation of the failure time with temperature.

375°C were conducted mainly in the stagnant gas mode. These tests started immediately after the inside of the tube was pressurized with hydrogen gas. Although any water vapor content inside the cladding tube was not observed in these experiments, it probably differed from run to run. Compared to data at 385°C and 20 ppmv water content, the results at 340°C and 375°C show greater scatter. This is attributed to the lack of control of the H_2O content of the gas in these tests. As discussed in the following section, hydriding susceptibility is very sensitive to water content.

3.2. Effect of water vapor content

The effect of water vapor content in hydrogen gas on hydriding at 385°C is shown in Fig. 5. The experiments were conducted in the flowing gas system with and without the water reservoir connected. As seen in the graph, hydriding occurred in H_2 with 20 ppmv water vapor ($H_2/H_2O = 5.0 \times 10^4$) but was suppressed at 80 ppmv ($H_2/H_2O = 1.25 \times 10^4$) and 120 ppmv water vapor ($H_2/H_2O = 8.3 \times 10^3$). Thus, hydriding, rather than oxidation, is the dominant reaction when the H_2/H_2O ratio exceeds a critical value of about 10^4 at 385°C. Kim et al. [9] investigated the effect of water content on hydriding in microbalance experiments and suggested that the critical values be 2.5×10^3 and 2.0×10^2 at 350°C and 400°C, respectively. The critical H_2/H_2O value obtained from the present study is higher than that of Kim. The reason for this difference is unknown. Operating temperatures and pressure are very similar in both studies but the chemical composition of the liner is different. The present specimen has Zr–0.15 wt% Fe alloy liner while the sponge-Zr liner was used in Kim's experiment. It is reported that improved oxidation resistance can be achieved by adding iron to sponge
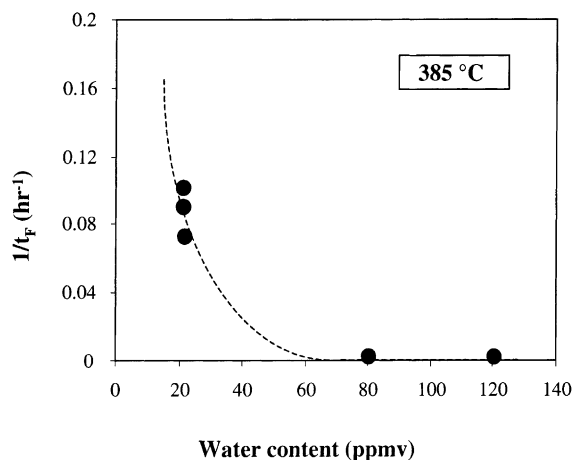
zirconium [14]. Since the liner in this study is more resistant to oxidation than sponge Zr, the oxide layer on it is thinner than on the sponge Zr liner. If the oxide layer is responsible for resistance to hydriding, then the liner with the thinner oxide should be more susceptible to
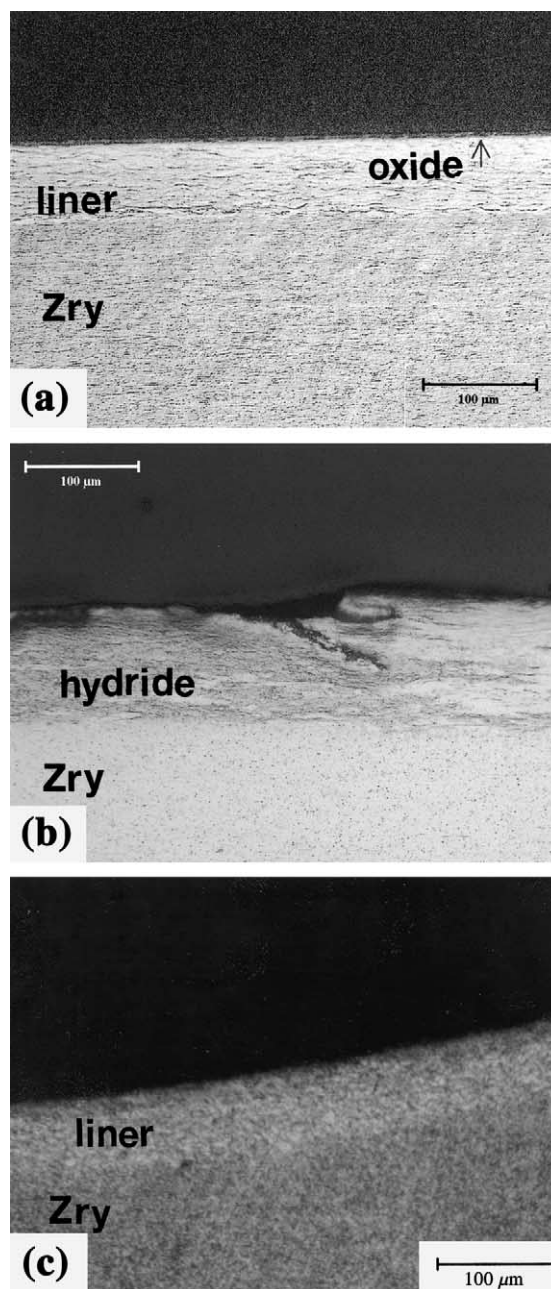

Fig. 6. Cross-sectional morphology of the heated section after the exposure to dry H_2 at 340°C: (a) SEM morphology of an etched specimen (intact); (b) SEM morphology of a non-etched specimen (hydrided); (c) optical morphology of a non-etched specimen (intact).

Fig. 5. Effect of water vapor content on the failure time at 385°C.

hydriding, leading a lower critical H_2/H_2O ratio. This argument leads to a conclusion contrary to the present results. Perhaps the oxide scale on the Zr–0.15 wt% Fe liner, although thinner, is more impervious to hydrogen penetration than the oxide on the pure-Zr liner. Alternatively, Takagi suggested that the absorption rate of hydrogen gas is related to the microstructure of Zry [15]. Although microstructures of the present specimens were unidentified, it is possible that some microstructural properties such as recrystallization, grain size and second phase particles caused the discrepancy in the critical H_2/H_2O ratios observed in the present study and in [9].

3.3. Surface condition

In order to determine if surface condition is a significant factor, three specimens were etched and hydriding characteristics were investigated at 340°C. All three survived in the 140-h exposure to hydrogen compared to failure of 5 of 10 specimens tested in the as-received condition (see Table 2).

A comparison of cross-sectional microstructures between an etched specimen and a non-etched specimen is shown in Fig. 6. Fig. 6(a) exhibits the SEM morphology of the heated post-test section of the one of the specimens that survived in the test at 340°C. The specimen had been etched prior to testing. Three distinct layers were observed. The outmost layer was revealed by Auger electron spectroscopy (AES) to be an oxide layer. The liner (middle layer) had not hydrided, indicating that the oxide layer is protective. A thin native oxide exists on the inner surface of the as-received cladding material. This oxide layer could have imperfections such as small cracks or scratches, which allowed hydrogen permeation through the layer during testing. However, etching provides a relatively clean metal surface and the new oxide layer formed on it during testing is protective, thereby enhancing hydriding resistance. Fig. 6(b) shows the SEM morphology of the non-etched specimen hydrided at 340°C. As seen in the figure, both liner layer and Zry were hydrided. Cracks were formed in the hydride layer and some parts of the hydride were flaked off. Fig. 6(c) exhibits the optical micrograph of the non-etched specimen that survived in the test. AES showed that a thin oxide layer exists at the surface of the specimen. Any hydride was not observed in this specimen as shown in the figure. The microstructure of the oxides was not studied in this study; however, these oxide layers seem to play the critical role of rendering the specimens immune from hydriding in the conditions of the test.

4. Conclusions

The tube-burst technique has provided reliable measurements of the high pressure hydriding resistance of Zry cladding at various temperatures. The transition temperature separating specimens that were non-reactive (survival time >140 h) and reactive is a characteristic measure that differentiates the different types of cladding materials. In dry H_2, the changeover from immunity to hydriding takes place over a very narrow temperature range around 340°C for the specimens tested in this study. Hydriding susceptibility was highly dependent on the water vapor content in hydrogen gas. The critical H_2/H_2O ratio was found to be about 10^4 at 70 bar and 385°C. The failure time provided by the tube-burst technique is a useful measure of the hydriding susceptibility of Zry cladding. The gas-flow mode of operation is more reliable than the stagnant gas mode chiefly because it allows for control of the water vapor content of the hydrogen gas.

References

[1] C.Y. Li, D.R. Olander, Rad. Phys. Chem. 54 (1999) 301.

[2] J.C. Clayton, in: Eighth International Symposium on Zirconium in the Nuclear Industry, ASTM STP vol. 1023, 1989, p. 266.

[3] D.R. Olander, S. Vaknin, Secondary hydriding of defected Zircaloy-clad fuel rods, EPRI TR-101773, 1993.

[4] R.L. Yang, O. Ozer, S.K. Yagnik, B. Cheng, H.H. Klepfer, N. Kjaer-Pedersen, P. Rank, EPRI failed fuel degradation R&D program, in: Proceedings of the International Topical Meeting on LWR Fuel Performance, West Palm Beach, FL, USA, American Nuclear Society, 1994.

[5] Y.S. Kim, W-E. Wang, D.R. Olander, High Temp.–High Press. 27&28 (1995–1996) 555.

[6] Y.S. Kim, W-E. Wang, D.R. Olander, S.K. Yagnik, J. Nucl. Mater. 246 (1997) 43.

[7] D.R. Olander, W-E. Wang, Y.S. Kim, C.Y. Li, S. Lim, S.K. Yagnik, J. Nucl. Mater. 248 (1997) 214.

[8] Y.S. Kim, W-E. Wang, D.R. Olander, S.K. Yagnik, J. Nucl. Mater. 240 (1996) 27.

[9] Y.S. Kim, W-E. Wang, D.R. Olander, S.K. Yagnik, J. Nucl. Mater. 245 (1997) 152.

[10] R.P. Marshall, J. Less-Common Met. 13 (1967) 45.

[11] S. Aronson, Some experiments on the permeation of hydrogen through oxide films on zirconium, WAPD-BT-19, 1960.

[12] K. Une, J. Less-Common Met. 57 (1978) 93.

[13] H.S. Hong, W-E. Wang, D.R. Olander, High pressure hydriding of Zircaloy cladding by the tube-burst technique, in: International Topical Meeting on LWR Fuel Performance, Park City, UT, American Nuclear Society, April 10–15, 2000.

[14] A. Seibold, E. Steinberg, H. Krug, K. Woods, Nucl. News 38 (1995) 36.

[15] I. Takagi, D. Kawasaki, N. Horiuchi, K. Iida, D.D. Lestiani, H. Fujita, K. Higashi, Effect of local heating on hydrogen absorption in Zircaloy tube, Annual Report of Quantum Science and Engineering Center, Kyoto University, Japan, 1999.