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Chemical processes in defective LWR fuel rods

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Abstract

The results of several experimental studies aimed at improving understanding of the chemical processes that cause severe degradation of defective light-water reactor fuel cladding are reported. The competition between oxidation and hydriding of zirconium and zircaloy exposed to steam–hydrogen mixtures at 70 bar and 350–400°C was studied by thermogravimetry. A critical H_2/H_2O ratio of the gas separates regimes of these two types of reaction. For sponge-Zr, the critical ratios at 350 and 400°C are ≈ 5000 and ≈ 200, respectively. Radiolysis of steam by alpha particles was studied mass spectrometrically. The yield of the hydrogen radiolysis product in saturated steam at 290°C was found to be ≈ 8 molecules per 100 eV of deposited energy. An in-reactor experiment demonstrated that fission-fragment-irradiated steam can oxidize UO_2 to UO_{2+x}.

1. Introduction

Secondary hydriding of zirconium-lined zircaloy (Zry) cladding following water ingress through a small primary defect is one of the major failure modes of BWR fuel. Fig. 1 summarizes diagrammatically the interacting chemical and physical processes that are set into motion by the opening of the rod interior to coolant. The reaction between steam and the sponge-Zr liner creates hydrogen in the fuel-cladding gap. Hydrogen production may be significantly enhanced by fission fragment recoil from the fuel into the gap, where water molecules are decomposed into H_2 and one or both of the oxidizing species O_2 or H_2O_2. The radiolytic hydrogen adds to that generated by steam corrosion of the cladding and thereby increases the potential for hydriding of the cladding. In addition, the oxidizing radiolysis products can cause accelerated oxidation of the fuel, resulting in increased fission product release from hyperstoichiometric urania and producing hydrogen as well.

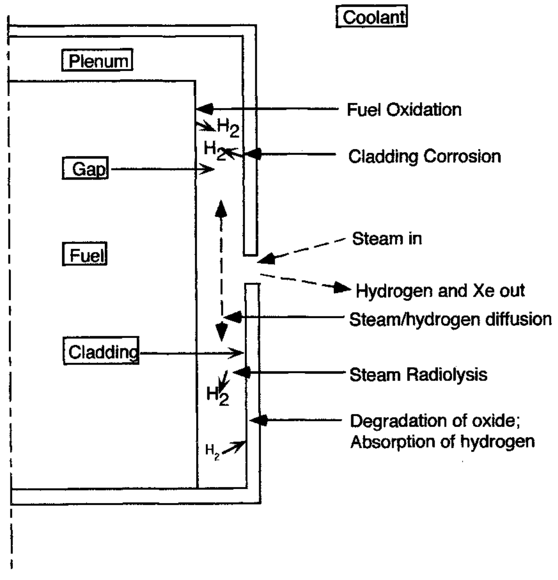

Fig. 1. Sources of hydrogen in a defective fuel rod.

At sufficiently high H_2/H_2O ratios in the gas in the gap, hydrogen can penetrate the oxide layer on the cladding wall and form zirconium hydride, which can lead to large-scale secondary failure (axial splitting) if the cladding is stressed at the location of the hydriding. Early attempts to quantify this process led to empirical rules-of-thumb intended to describe conditions conducive to massive hydrid-

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ing [1,2]. The most recent review of the topic is that of Clayton [3].

Severe cladding failures attributable to secondary hydriding are mainly, but not exclusively, observed in BWR fuel elements with a sponge-zirconium liner, which is often called 'barrier' cladding [4–6]. The soft sponge-Zr liner is a remedy for pellet–cladding interaction, but because it oxidizes more readily in steam than does zircaloy, is a more prolific hydrogen producer when the fuel rod is opened to the coolant by a small primary defect.

Most laboratory experiments aimed at quantitatively describing the kinetics of the hydriding process have been conducted at atmospheric or sub-atmospheric pressures [7–9]. The purpose of this paper is to report a few salient features of the hydriding reaction in 70 bar hydrogen–steam mixtures. This work is part of a program sponsored by the Electric Power Research Institute intended to provide a database for the computer code DEFECT [10], which is designed to predict the locations of axial zones in a defective fuel rod that are susceptible to accelerated hydriding.

The laboratory program consists of two components. The first is investigation, in a pressurized thermogravimetric apparatus (TGA), of the conditions for and the kinetics of hydriding of barrier cladding. The second is the study of the radiolysis of steam by heavy ions. In both experiments, temperatures and steam–hydrogen conditions (total pressure and H_2/H_2O ratio) are those that exist in the gap of a defective BWR fuel rod. Two conditions could not be simulated in the laboratory: the first is the energy deposition rate in the gas by recoiling fission fragments (alpha radiation was used instead). To rectify this deficiency, a test intended to reveal the consequences of steam radiolysis under reactor conditions was conducted in the Halden test reactor. The second is the limited quantity of hydrogen available in the closed gap of a defective fuel rod. To simulate this in the pressurized TGA tests, provision was made for rapidly increasing the water content of the gas contacting the specimen.

2. Experimental

2.1. High-pressure TGA

In the pressurized TGA experiment (Fig. 2), simulated barrier-cladding specimens were suspended from a microbalance by a wire terminating in a small furnace through which the H_2O/H_2 gas mixture flowed. The steam concentration in the gas was controlled by injecting water directly to the flowing hydrogen entering the furnace. During the experiments, the weight of the specimen was continuously monitored to provide on-line hydriding kinetic data. Details of the apparatus, with emphasis on the means of overcoming the deleterious effects of natural-convection flows of the gas, are given in a separate publication [11]. Further information can be found in Ref. [12].

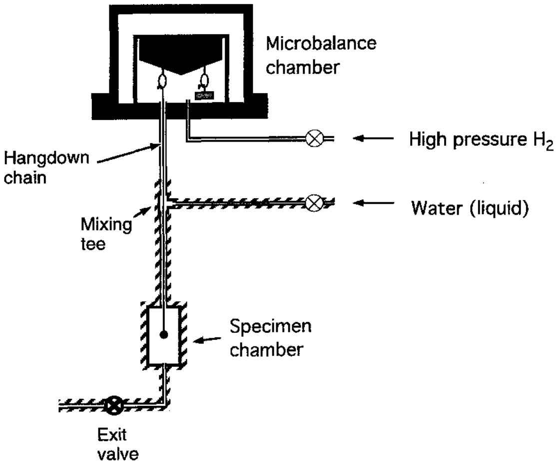

Fig. 2. Pressurized thermogravimetric apparatus.

Actual barrier-cladding tube sections could not be used in the experiments because the different chemical reactivities of the sponge-Zr liner and the zircaloy (Zry) outer surface cannot be distinguished by a single measure of reactivity (i.e., the weight gain). To avoid this difficulty, disk specimens (≈ 0.5 g) were cut from a specially fabricated plate of 1 mm thick Zry on which layers of ≈ 70 μm thick sponge-Zr were coextruded on both sides. The Zr/Zry/Zr sandwich plate was fabricated by Teledyne Wah Chang. Although the sandwich-plate configuration simulates the surfaces of Zr-lined Zry cladding tubes, it has edges which are not present in actual cladding. Because of the different densities of oxide, hydride, and metal, premature oxide or hydride film cracking at sharp edges is unavoidable. To avoid the deleterious effect of the edges, these regions were coated with a thin layer of pure gold. All specimens were pickled, and some were oxidized prior to testing to provide surface ZrO_2 scales of known thickness ('prefilmed' specimens). Following each experiment, the specimens were sectioned, mounted, polished, etched, and examined microscopically to reveal oxide or hydride morphology. The hydrogen content of the reacted specimens were determined with a simple home-built gas extraction apparatus [13].

2.2. Alpha-particle radiolysis apparatus

The laboratory radiolysis experiment (Fig. 3) consisted of exposing a small closed volume (6 cm^3) of saturated steam at 290°C to alpha radiation from a 5 mCi ^{244}Cm source. This irradiation chamber was connected to a reservoir of liquid D_2O which was not exposed to the alpha radiation. The irradiation chamber was attached to a mass spectrometric detection system via a high-temperature valve (V_1 in Fig. 3). All interior surfaces exposed to irradiated

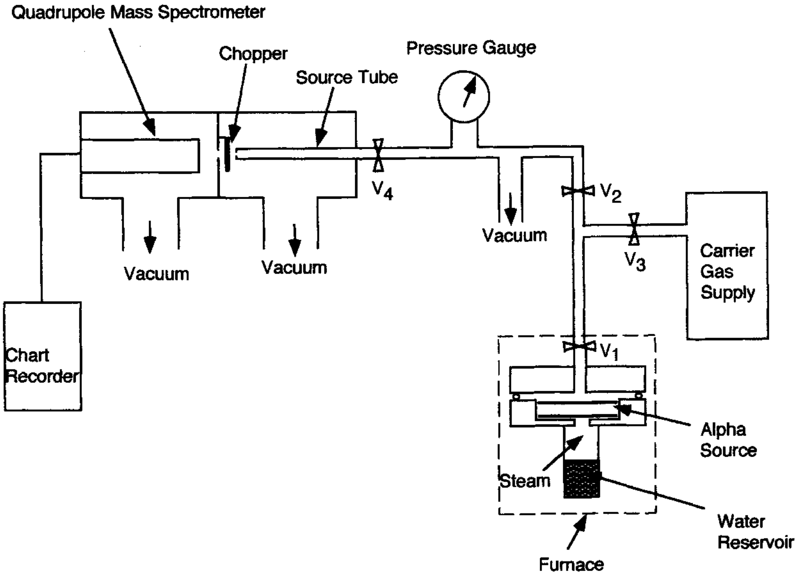

Fig. 3. Alpha-particle radiolysis apparatus with mass spectrometric detection.

steam were gold-plated to minimize wall reactions of the radiolysis products. Details of this experiment are given in Ref. [14].

After irradiation for times ranging from 10 to 100 h, D_2 produced by radiolysis of the D_2O steam was mixed with a larger (known) quantity of H_2 to avoid loss of deuterium by adsorption on metal surfaces. The mass spectrometer measurement of the D_2/H_2 ratio gave the quantity of D_2 produced by radiolysis. Division of this result by the energy deposited by stopping of the alpha particles in the steam gave the 'G value', which is the number of molecules of the product (D_2) per 100 eV of deposited radiation energy. This experiment was conducted in pure steam only; it could not be applied to steam–hydrogen mixtures because extensive isotope mixing rendered the dilution technique used in the pure steam measurement invalid. Instead, the effect of hydrogen in the steam was studied by irradiating a mixture of H_2 and $H_2{}^{18}O$ and measuring the G value of $^{18}O_2$.

2.3. Test-reactor radiolysis capsule

The in-reactor experiment conducted in the Halden reactor was designed to determine the effect of the products of steam radiolysis on oxidation of initially stoichiometric UO_2. Saturated steam at 290°C sustained by a liquid–water reservoir was irradiated by fission fragment recoils inside small capsules containing disks of UO_2 (see Fig. 4). To supply the fission-fragment flux, the surfaces of the UO_2 disks were coated with a thin deposit of highly enriched UO_2 (43% ^{235}U). The dose rate from this source was ≈ 5000 times higher than that provided by the alpha radiation in the laboratory radiolysis experiment and the irradiation time was 25 days instead of tens of hours. The holes drilled in the UO_2 disks permitted easy circulation of the irradiated steam to both sides of the specimens. Because of the ≈ 0.5 mm thick steam layers separating the UO_2 disks from the steel capsule wall, removal of fission heat from the disks was poor. Provision of adequate heat removal capacity is the reason for the inclusion of the copper-bar heat sink and the spring in the water reservoir at the bottom of the capsule. The disks were separated from each other by a 1 mm thick gold O ring and from the metal heat-sink surfaces by 0.5 mm thick gold O rings. The external surface of the capsule was cooled by saturated steam at 290°C.

In the in-reactor test, direct measurement of the products of steam radiolysis was not possible. Instead, oxidation of the fuel specimens was determined by the weight change before and after irradiation.

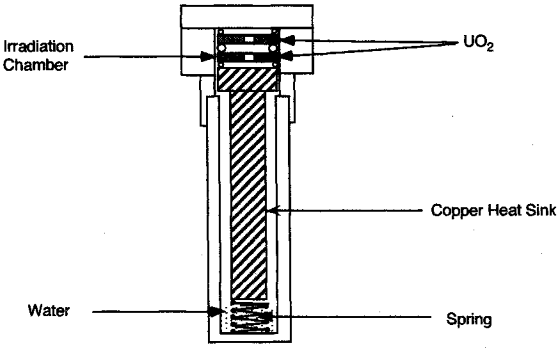

Fig. 4. Capsule for insertion in the Halden reactor to investigate UO_2 oxidation by irradiated steam.

3. Results

3.1. Thermogravimetric tests

The variables in the TGA experiments included temperature (350 and 400°C); H_2/H_2O ratio of the gas (5 to 10^5); oxide prefilm thickness (0 to 10 μm); substrate metal (crystal-bar Zr, sponge-Zr or Zry); and total gas pressure (1 and 70 bar). The last two variables were tested in 400°C pure hydrogen only, and the results are reported in Ref. [15]. A brief summary of these results is: (i) for all substrate metals, the rate of hydriding in 70 bar H_2 is ≈ two orders of magnitude higher than in H_2 at 1 bar pressure; (ii) contrary to oxidation, Zry hydrides more readily than sponge-Zr, as evidenced by both microscopic examination and weight-gain measurements; (iii) 'sunburst'-type hydriding, often observed in hydrided fuel rods, was occasionally produced in the laboratory tests. However, most hydriding morphology consisted of heavily hydrided surface layers and hydride platelets in the specimen interior. The effects of temperature, prefilm oxide thickness, and H_2/H_2O ratio of the gas are discussed below.

Based on the rate of hydrogen absorption, two modes of hydriding were observed. The first was characterized by very rapid hydrogen uptake rates, on the order of 10^{-7} mol H/cm^2s at 70 bar. This is classic 'massive' hydriding. The second form is termed 'slow' hydriding, and occurred at a rate about an order of magnitude smaller than that of massive hydriding. The weight gain rates associated with either of these modes of hydriding were much larger than those observed when only oxidation occurs, so distinguishing between hydriding and oxidation was straightforward. The slow hydriding process occurs only when conditions for hydriding and oxidation were roughly equally favorable (i.e., at the 'critical' H_2/H_2O ratio). Fig. 5 shows an experiment in which slow hydriding occurred for ≈ 1 h and was followed by a transition to massive hydriding.

The effect of prefilming the metal with an oxide layer was mainly to change the period over which slow (or no) hydriding occurred. Fig. 6 shows this effect clearly; in nearly pure hydrogen, the larger the prefilmed oxide thickness, the longer the incubation period prior to the onset of massive hydriding. In this case, no amount of prefilming can prevent massive hydriding of the specimen; at most it can delay it. However, when the H_2/H_2O ratio is near a 'critical' value, the role of the oxide prefilm is more complicated. The effect of prefilming is longer monotonic; thick films (≈ 10 μm) offer poorer hydriding resistance than thin films (1 to 2 μm). For hydrogen–steam ratios above the critical value, hydriding occurs no matter what the prefilm oxide thickness. For ratios below the critical value, only slow oxidation takes place. At 70 bar total pressure, the critical hydrogen-to-steam ratios were ≈ 200 at 400°C and ≈ 5000 at 350°C. A distinct 'critical' ratio does not really describe the process. Rather, the transition from hydriding to oxidation occurs over a range of H_2/H_2O ratios whose center can be loosely called a critical ratio. In this range, the presence of a previously deposited oxide layer on the surface can significantly affect the chemical response of the metal. On either side of the transition range, the oxide prefilm thickness is much less important. On the hydrogen-rich side, the prefilm thickness provides a short incubation period and on the steam-rich side, it has no effect at all on hydriding because oxidation is the only reaction taking place.

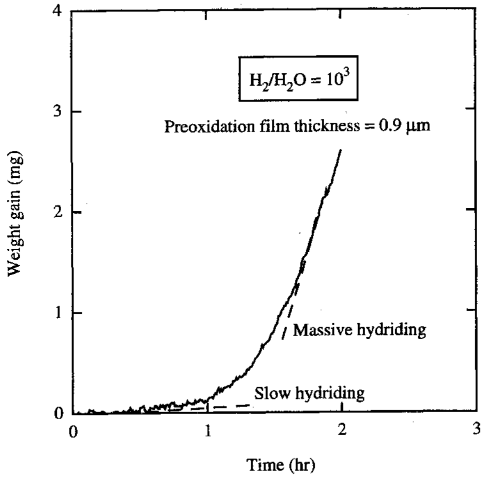

Fig. 5. Hydriding of sponge-Zr at 400°C and 70 bar in a gas with $H_2/H_2O = 10^3$.

Once started, massive hydriding rapidly consumed the entire specimen, behavior that is quite different from in-reactor hydriding that produces numerous spots or sunbursts of hydride. This in-reactor behavior is attributed to hydro-

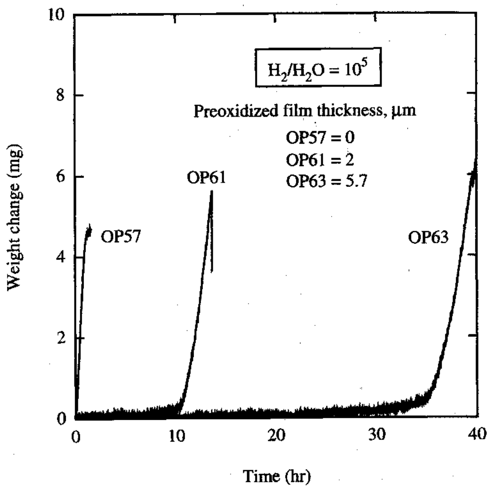

Fig. 6. Hydriding of sponge-Zr at 400°C and 70 bar with $H_2/H_2O = 10^5$ (commercial-grade hydrogen).

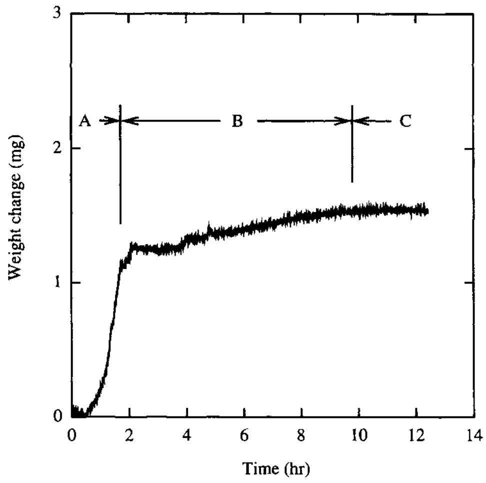

Fig. 7. Initiation and termination of massive hydriding of the Zr/Zry/Zr sandwich specimen at 350°C and 70 bar. Region A: massive hydriding ($H_2/H_2O = 10^5$); region B: retardation of massive hydriding ($H_2/H_2O = 10^3$); region C: termination of massive hydriding ($H_2/H_2O = 2 \times 10^2$).

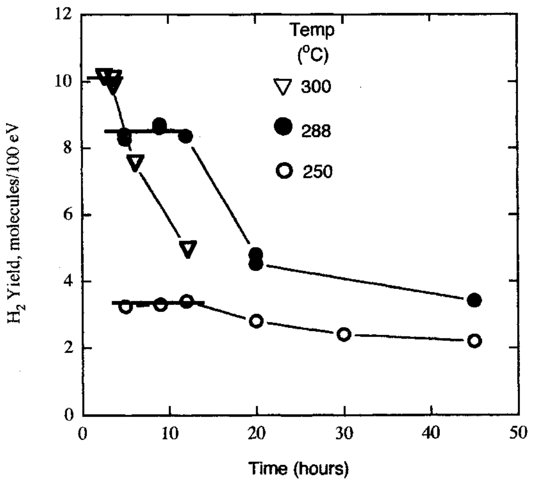

Fig. 8. Yields of hydrogen from radiolysis of pure saturated steam at various temperatures as functions of irradiation time.

gen starvation due to the small gas volume in a closed fuel-cladding gap. To terminate hydriding in the laboratory experiments, steam was injected into the gas during massive hydriding that had begun in gases with H_2/H_2O ratios above the critical value. As shown in Fig. 7, this method proved effective and suggests that the hydrogen-starvation mechanism is operative in defective BWR fuel rods.

The above results apply to sponge-Zr surfaces on Zry substrates. A few experiments were performed with standard Zry. As long as the oxide layers are coherent, the initial rate of steam oxidation of Zry is not too different from that of sponge-Zr. The difference is that the rate of sponge-Zr oxidation remains constant while that of Zry decreases with time. However, sponge-Zr has the potential for undergoing much more rapid oxidation that is signaled by the appearance of white particulate matter on the surface or even of oxide flaked completely from the specimen. These white oxide coats are not protective against hydriding [16].

3.2. *Alpha-particle radiolysis of steam*

As shown in Fig. 8, the alpha-particle radiolysis experiments yielded initial *G* values for hydrogen production from pure saturated steam of the order of 8 molecules per 100 eV at typical in-reactor temperatures. With increasing dose (or time), the *G* value decreased as radiation equilibrium was approached. The temperature effect seen in this figure is in reality a steam-density effect. This was proved by a 288°C irradiation of superheated steam with a density equal to that of saturated steam at 250°C. The hydrogen yield for this test (which is not shown in Fig. 8) was about two, which is the same as the saturated steam test at 250°C [14].

The *G* values for oxygen production were ≈ 1/8 those for hydrogen, suggesting either that some H_2O_2 was produced (and not detected) or that radiolytic oxygen reacted with metallic surfaces even though the irradiation chamber had been gold-plated. Addition of a few percent hydrogen to the steam dramatically reduced the oxygen yield. It is not known whether this results from depression of the net decomposition rate of water or from conversion of some of the oxygen product to H_2O_2. No hydrogen peroxide could be detected by standard wet-chemical methods in the chamber water after irradiation.

3.3. *In-reactor tests*

Table 1 shows the conditions and the results of Halden in-reactor capsule irradiations. The UO_2 disks in capsules 1 and 2 had 43% enriched UO_2 (HEU) layers on their surfaces, so the steam next to the oxide was subjected to high fission-fragment fluxes. Specimens 1 and 2 differed chiefly in the UO_2 temperature during irradiation, achieved by the different uranium enrichments. The disk tempera-

Table 1
Halden capsule irradiation of initially stoichiometric UO_2 disks

Capsule No.	1	2	3
U enrichment of disks (%)	0.3	0.71	0.3
HEU layer	yes	yes	no
Fission-fragment energy flux (W/cm^2)	0.84	0.84	0.01
Heat flux (W/cm^2)	5.3	8.0	2.0
Disk temp. (°C)	560–830	700–1100	400–500
Final O/U ratio	2.04	2.02	2.005

tures in Table 1 were calculated from the heat sources in the capsule, and the ranges of temperatures shown are due to the effect of including natural convection in the heat transfer analysis. The initially black UO_2 specimen surfaces were completely brown in color when removed after irradiation.

The results showed that the fuel was oxidized in the presence of radiolyzed steam. The final O/U ratios of the fuel disks (bottom row of Table 1) ranged from 2.005 to 2.04. The control test (capsule 3) had no HEU source and showed practically no weight gain. The disk operating at the highest temperature (capsule 2) showed less oxidation than the one that was at a lower temperature (capsule 1). Because of cracking of some of the disks during handling of the capsules, the extends of oxidation inferred from the specimen weight gains must be viewed as preliminary. Hot-cell gravimetric O/U measurements will be performed on the specimens to corroborate the gross weight-gain results.

4. Conclusions

Pressurized TGA experiments on sponge-Zr have provided reliable measurements of the critical H_2/H_2O ratio for the onset of massive hydriding at 70 bar pressure. This ratio increases as the temperature decreases. Sponge-Zr produces a less-protective oxide than Zry, but the latter hydrides more readily than the former.

The large *G* value for hydrogen in pure steam observed in laboratory experiments suggests that radiolysis may be an important source of H_2 in a defective fuel rod. The in-reactor tests showed that steam radiolysis products are capable of oxidizing UO_2 under BWR conditions.

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