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High-temperature absolute hydrogen desorption kinetics of zirconium hydride under clean and oxidized surface conditions

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ABSTRACT

High-temperature absolute hydrogen desorption kinetics of zirconium hydride specimens with H/Zr ratio from 1.7 to 0 with no hydrogen backpressure for oxidized and clean surface conditions were discussed. The temperature under study was in the range of 750–820 °C in order to create a hypothetical reactor accident condition manageable by the experimental setup. For the case of the clean surface state, hydrogen release was so rapid that most of hydrogen had escaped from zirconium hydride specimens over the course of only 10 min in the temperature range of ~600–700 °C. For the case of the oxidized surface condition, the release rate was much slower and exhibited a strange and unexplainable linear fashion regardless of the temperature and H/Zr ratio. The zeroth-order absolute dehydriding rate was determined with an activation energy of 313 ± 17 kJ mol^{-1}.

1. Introduction

The current fuel for commercial light-water reactor is made of uranium dioxide (UO_2). There have been a number of proposals to switch from UO_2 to uranium zirconium hydride (UZrH) because of several advantages [1–3]. First, the amount of water needed as a moderator would be lower, resulting in a size reduction of water channel in the fuel assembly. This would result in the reactor core being able to accept more fuel allowing for higher power density. This feature is achievable because hydrogen atoms that act as a moderator are incorporated directly into the fuel inside the fuel rod, whereas for the conventional fuel, the moderator stays outside of the fuel rod. Second, the hydride fuel exhibits a large prompt negative temperature coefficient of reactivity [2], which means that if fission reaction and fuel temperature increase rapidly, the hydrogen up-scattering accompanying the Doppler effect would result in an immediate automatic shutdown of the reaction. This feature makes the fuel very attractive in the view of safety characteristics. In fact, this inherent safety feature of the hydride fuel has been employed in General Atomics' TRIGA research reactors worldwide, permitting them to successfully perform the unique transient power pulsing and allowing the reactors to operate worldwide for more than 45 years without any accident related to fuel over-heating [4]. In addition, the United States of America successfully used the UZrH fuel in small nuclear reactors for SNAP programs. Third, the hydride fuel offers a superior thermal conductivity and fission gas retention capability, although it suffers higher fuel swelling [1]. Fourth, upgrading the commercial fuel from UO_2 to UZrH presents several economic improvements for commercial nuclear power stations [10].

The structure of uranium zirconium hydride fuel composes of a separate metallic uranium phase embedded into a solid zirconium hydride matrix. $UZrH_{1.6}$ with U:Zr ratio of 30:70 was determined to be the optimal fuel stoichiometry for use in power reactors [1]. Fig. 1 shows a photomicrograph of the fuel. The dark and light regions represent uranium and zirconium hydride phases, respectively.

Fig. 2 depicts a Zr–H phase diagram with H_2 isobars. During normal operation, hydrogen atoms at the surface of the fuel establish a thermodynamic equilibrium with the hydrogen gas in the pellet–cladding gap according to the Wang–Olander equation [8,9]:

$$\ln(p) = 2\ln\left(\frac{C}{2-C}\right) + 8.01 + 5.21C - \frac{2.0\times10^4}{T} \qquad (1)$$

where p is the hydrogen partial pressure in atmosphere, C is the surface H/Zr ratio, and T is temperature in Kelvin.

The hydride fuel surface temperature is calculated to be approximately 510 °C for conventional fuel rod with pressurized He gas, and ~385 °C for liquid–metal-bonded fuel rod where a Pb–Sn–Bi low-melting alloy replaces He in the gap [1]. This results in the H_2 partial pressure inside the fuel rod of no more than 10^{-3} atm. Therefore, hydrogen gas pressure inside the fuel rod under normal operation poses no danger whatsoever (albeit that hydrogen will be absorbed into the Zry cladding where it can form brittle hydride

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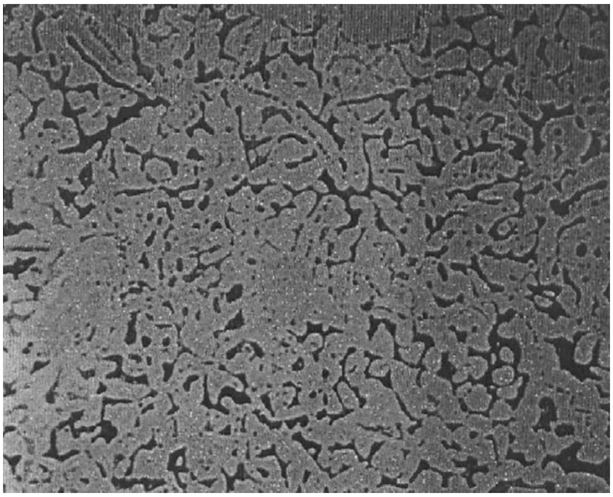

Fig. 1. Photomicrograph of the hydride fuel. The dark and light regions represent uranium and zirconium hydride phases, respectively [5].

platelets after a sufficient quantity of hydrogen in the cladding is collected).

A potential problem exists when changing from UO_2 to $UZrH_{1.6}$ fuel, where during postulated transient power increase conditions the fuel temperature could increase significantly to, for example, 1100 °C.[1] Extrapolation of H_2 isobars in the phase diagram in Fig. 2 reveals the new equilibrium hydrogen pressure inside the fuel rod of tens of atmospheres. This may affect fuel rod integrity, potentially leading to fuel rod bulging or even rupture. Moreover, hydrogen gas in the gap would diffuse back into the fuel at colder regions (e.g., at the top and bottom of the 4-m long fuel rod), causing an uneven hydrogen stress along the axial direction of the fuel rod. Therefore, information on hydrogen release behaviors, specifically the absolute desorption kinetics, is of critical importance for the safety analysis and certification of the fuel before it can be put into commercial service. This paper discusses high-temperature absolute hydrogen desorption kinetics of zirconium hydride with H/Zr ratio from 1.7 to 0 with no hydrogen backpressure for oxidized and clean fuel surface conditions. The temperature under study was in the range of 750–820 °C in order to create a hypothetical reactor accident condition manageable by the experimental setup. Uranium was not used in the experiment because uranium and zirconium hydride exist as separate phases and because the presence of uranium reduces U–Zr phase diagram temperatures by only a few degrees [4].

2. Experimental setup

2.1. Zirconium hydride synthesis

Zirconium hydride tube specimens were synthesized in a Thermogravimetric Analyzer (TGA). Fig. 3 demonstrates a schematic drawing of the experimental setup.

The TGA system consists of a specimen chamber connected to a microbalance weighting cell chamber. In the stainless steel specimen chamber, various gases can be supplied through gas flow meters and gas filters. Steady temperature environments can be maintained using a typical clamp–shell-type high-temperature furnace installed around the chamber and wrapped with a thick layer of insulating material. High vacuum can be created inside the chamber by using a combination of mechanical and turbomolecular pumps. The specimen is suspended inside the chamber using a small corrosion-resistant Pt–Rh wire. Signals from the microbalance chamber representing the weight change of the specimen are recorded on a computer through a data acquisition board.

Nuclear-grade Zry-4 tubes were sectioned into small pieces, each about 1.5 cm in length. The specimens were chemically-etched by dipping into a 50% HNO_3 + 45% H_2O + 5% HF etching solution for approximately 2 min to remove native oxide layer. Each of the tubes was suspended inside the stainless steel reaction chamber, which was then evacuated of air, reaching a pressure of $\sim 10^{-3}$ Torr. After maintaining the vacuum for a few minutes, ultra-high purity argon gas, further purified through a gas filter to scavenge remaining oxygen and moisture, was released into the chamber at 1 atm and the temperature was slowly raised to the desired value (~500–700 °C depending on each run). Ultra-high purity hydrogen gas, further purified through the gas filter, was subsequently released into the chamber. The weight change of the specimen resulting from hydrogen absorption was tracked real-time on a computer connected to the TGA. When the desired H/Zr ratio was obtained, the furnace was rapidly removed from the reaction chamber in order to quench the sample and stop any further hydrogen gain or loss from the fuel. Concurrently, the hydrogen gas supply was stopped and the argon gas flow rate was increased in order to quickly purge the remaining hydrogen gas. Zirconium hydride tubes with various H/Zr ratios in the range of 1.50–1.70 were successfully synthesized. Fig. 4 illustrates examples of successfully synthesized zirconium hydride specimens and the associated H/Zr ratios.

2.2. Absolute hydrogen desorption kinetics

To determine the absolute kinetics of hydrogen release from zirconium hydride, an appropriate specimen was again hung inside the reaction chamber. Chemically-etched specimens following zirconium hydride synthesis were used to determine the absolute kinetics under a clean surface condition, while as-synthesized specimens were used to determine the absolute kinetics under an oxidized surface condition. After the chamber was tightly closed, it was quickly evacuated of air, achieving a pressure of $\sim 10^{-3}$ Torr. The temperature was quickly raised to 750–820 °C depending on each run and maintained at a constant value throughout the run. The weight loss curve was recorded and analyzed.

To clarify the extent of oxidation, surfaces of specimens after successful hydrogenation appeared slightly darker than those immediately before being loaded into the specimen chamber. This is because during hydride processing, the system would never be absolutely oxygen-free. Some trace amount of oxygen gas must still be present in the chamber in sufficient concentration to form a very thin oxide layer at elevated temperature (which was not thick enough to effectively prevent hydrogen diffusion into zirconium surface). After the specimen was removed from the chamber, oxidation slowly continued to take place at room temperature to form a thick native oxide layer identical to those on zircaloy tubes before chemical etching. Fig. 5a illustrates a scanning electron micrograph showing a ~1–2 μm thick oxide layer of a typical oxidized surface specimen. Fig. 5b displays an approximately <0.5 μm thick oxide layer of a typical clean surface specimen. The oxide layer appears as a white layer in the micrographs.

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[1] The basis for this postulated accident temperature is derived from the following three sources: (1) Lindgren and Simnad reported quench tests of TRIGA fuel where specimens with the size similar to a BWR UO_2 fuel pellet were heated up to 1200 °C [11]; (2) Simnad puts the maximum TRIGA fuel temperature ever experienced during a pulsing experiment at 1150 °C [Simnad, 1981]; (3) according to the information on General Atomics company website, the UZrH fuel can be safely quenched at 1200 °C in water (http://www.gaesi.com/triga/about/index.php, accessed March 20, 2010).

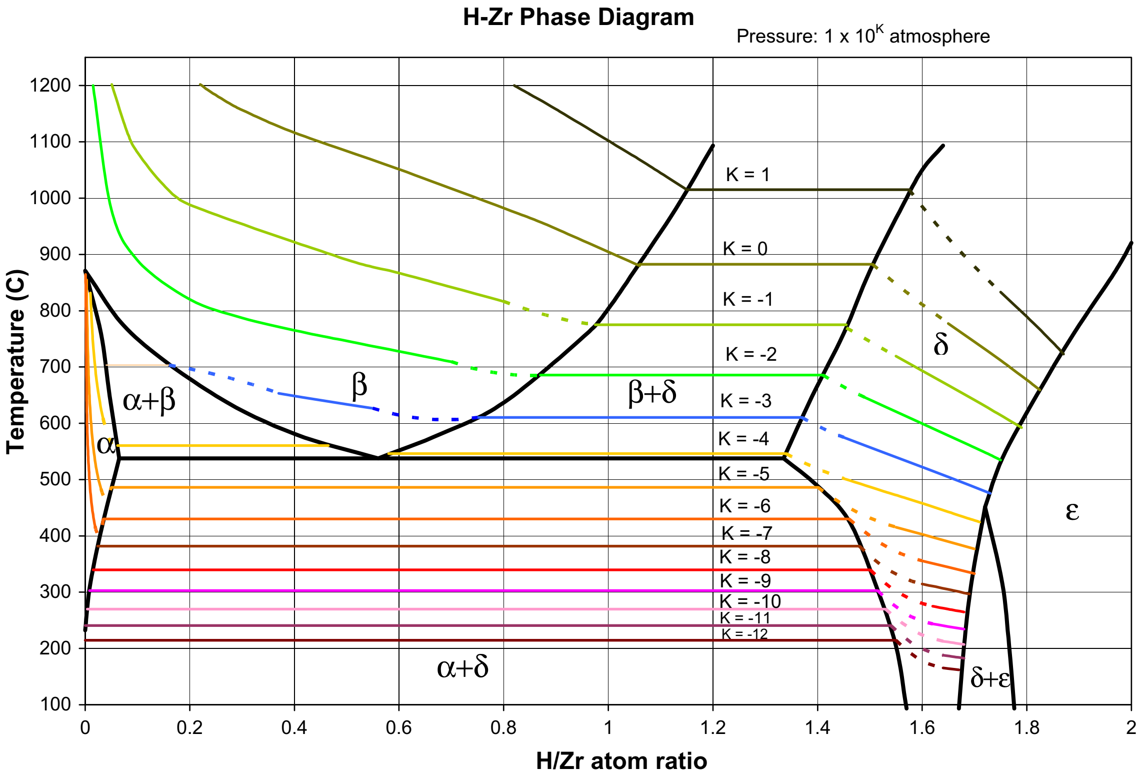

Fig. 2. Zr–H phase diagram with H_2 isobars ($pH_2 = 10$ K atm) [6,1].

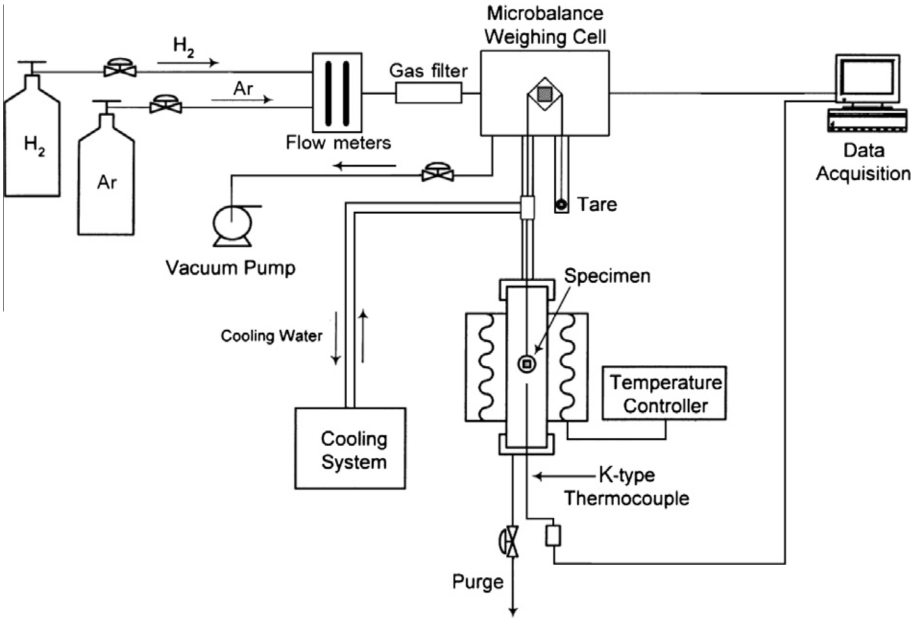

Fig. 3. Drawing of the experimental setup.

3. Results and analysis

3.1. Clean surface condition

Typical weight loss curve and temperature history for the clean surface situation are presented in Fig. 6.

The kinetics of hydrogen desorption was so rapid that essentially most of the hydrogen had escaped from zirconium hydride specimen during the course of the temperature ramp. Because of this, the absolute release kinetics at a constant temperature cannot be accurately obtained. Quantitatively speaking, the entire hydrogen release from zirconium hydride tube was completed over the course of only 10 min in the temperature range of ~600–700 °C. This new finding suggests the following: if a hypothetical severe accident takes place that results in the fuel temperature rising to more than 800 °C for a prolonged duration, the zircaloy cladding

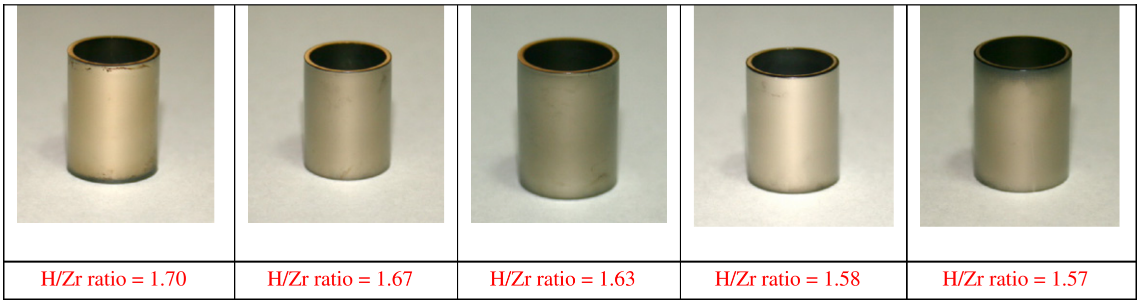

Fig. 4. Examples of successfully synthesized zirconium hydride tubes and the associated H/Zr ratios.

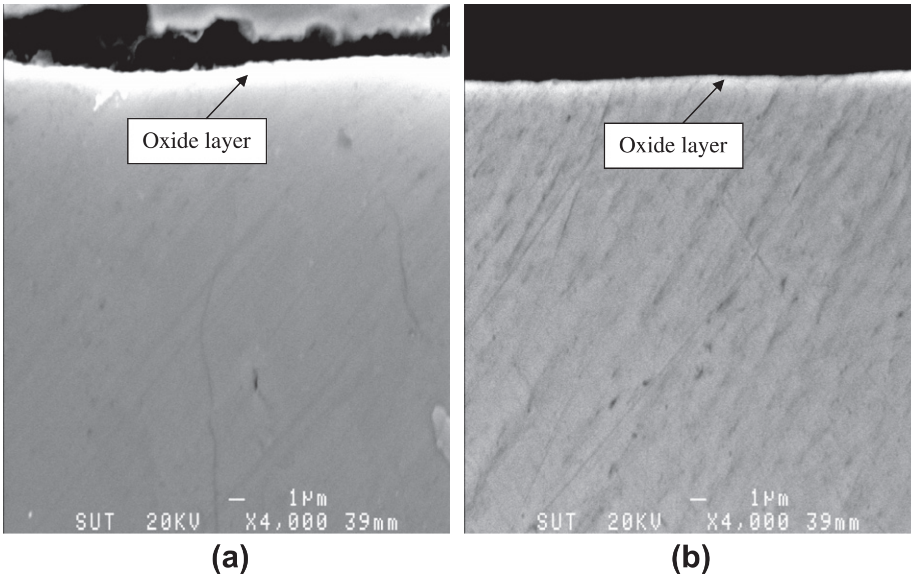

Fig. 5. Scanning electron micrographs showing oxide layers of specimens for hydrogen release analysis: (a) under oxidized surface condition and (b) under clean surface condition.

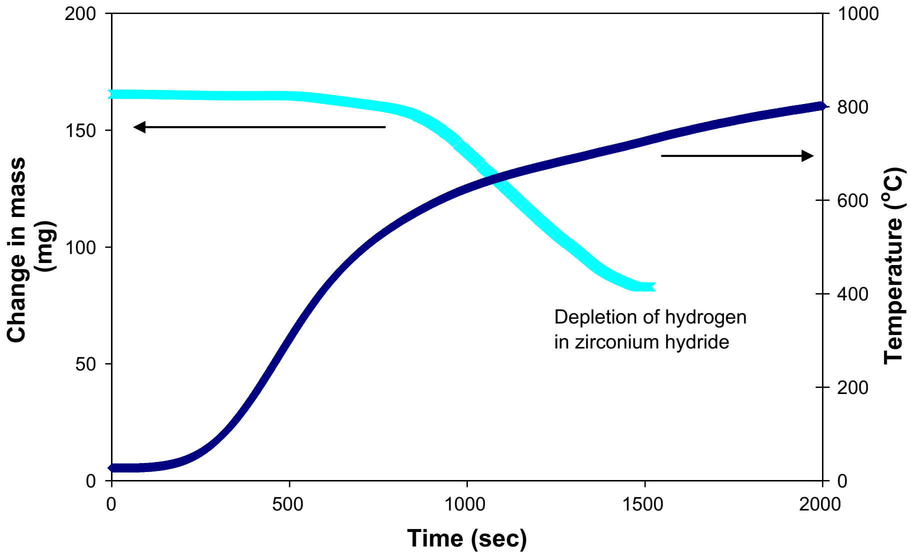

Fig. 6. Typical weight loss curve and temperature history for the clean surface condition.

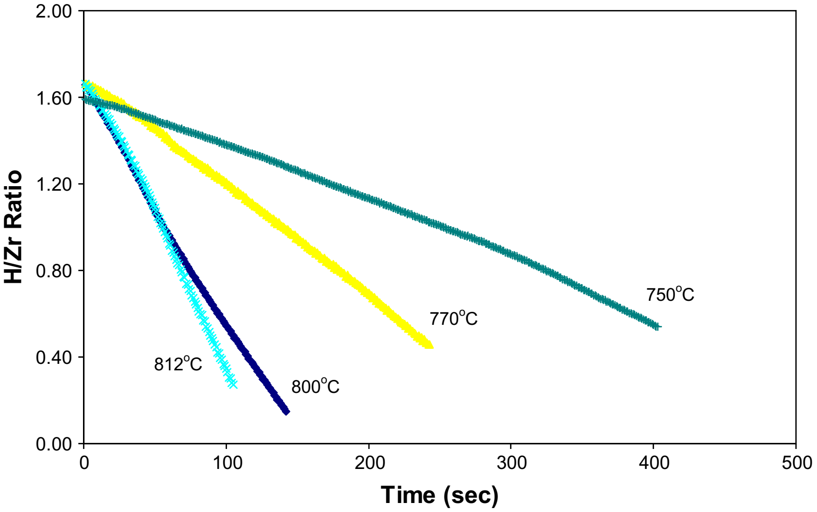

Fig. 7. Typical weight loss curves for the oxidized surface condition ($t = 0$ s did not correspond to the start of the temperature ramp).

would first be destroyed [3]. Subsequently, rapid hydrogen release[2] would (at least initially) take place from newly-formed oxide-free surfaces and large cracks in fuel pellets fallen to the bottom of the reactor pressure vessel (RPV).[3] This would result in a large collection of hydrogen gas at the top of the RPV in a relatively short period of time, possibly exceeding the capacity of the hydrogen igniters and recombiners installed at the top of the RPV. Under suitable conditions, the built-up hydrogen gas could ignite uncontrollably all at once, potentially resulting in catastrophic damages to the core internals and the RPV. Moreover, hydrogen gas could displace the remaining coolant in the reactor core, potentially causing a reactor meltdown.

3.2. Oxidized surface condition

Compared to the case of the clean surface condition, hydrogen release from an oxidized surface was not rapid as most of hydrogen was still retained in zirconium hydride when the temperature reached a final value. This obvious outcome stems from the fact that an oxide layer acts as an effective barrier to hydrogen desorption. Fig. 7 depicts typical weight loss curves during a constant temperature portion. Note that, in contrast to Fig. 6, $t = 0$ s does not correspond to the beginning of the temperature ramp. It corresponds to the start of hydrogen loss at constant temperature. The starting H/Zr ratio was slightly different for each curve because zirconium hydride tubes were synthesized having the H/Zr ratio in the range of 1.50–1.70.

The weight loss curve for every run was surprisingly linear, signifying a zeroth-order reaction kinetics essentially throughout the entire H/Zr range. In other words, the release rate is independent of the H/Zr ratio. This peculiar result is identical to what Gutkowski found [7] during his similar experiments but at lower temperature. As discussed by Olander [3], two processes occurring in series control the reaction kinetics: the solid-state diffusion of hydrogen in zirconium hydride to the free surface, and the recombination of hydrogen atoms at the fuel surface to form hydrogen gas. For either of the steps, the rate should have decreased with time. The results found earlier by Gutkowski and discovered in this study (at higher temperature range) confirm this strange behavior.

The absolute dehydriding rate, k (mmol H/cm^2 s), was determined in the following way:

1. The slope of the dehydriding curve was determined.
2. The unit “H/Zr ratio per second” was converted into “moles of hydrogen atoms released per second” by multiplying with an appropriate conversion factor to change the H/Zr ratio to moles of hydrogen released.
3. The quantity was then divided by the surface area of the Zry-4 tube specimen to obtain the final unit of mole H/cm^2 s.
4. The k value for each temperature was determined.

Absolute dehydriding rates at various temperatures were plotted on a conventional Arrhenius plot illustrated in Fig. 8. Another set of data obtained by Gutkowski [7] on similar experiments performed at a lower temperature range was included. Both sets of data reside on the same linear trend line, signifying an exceptionally good agreement. Using the trend line, k was determined to be:

$$k = \exp\left(31.1 \pm 2.0 + \frac{-313 \pm 17\ [\mathrm{kJ\ mol^{-1}}]}{RT\ [\mathrm{K}]}\right) \quad (\mathrm{mmol\ H/cm^2\ s}) \tag{2}$$

with an activation energy of 313 ± 17 kJ mol^{-1}.

Following the hypothetical severe accident condition discussed in Section 3.1, newly-formed surfaces and large cracks on fuel pellets would eventually become oxidized to the extent that hydrogen release would be sluggish. If the oxidation progresses quickly, the total quantity of liberated hydrogen gas would not be so large, possibly allowing the hydrogen igniters and recombiners to safely control and manage.

3.3. Comparison of mass losses under oxidized and clean surface conditions

In order to better examine the difference of hydrogen loss rates between the two surface conditions, the rate at each temperature was calculated using Eq. (2) and the temperature curve in Fig. 6. The result was numerically integrated to provide the hydrogen

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[2] For perspective, this analysis assumes a He-filled fuel rod. For the case of a liquid–metal-bonded fuel rod, hydrogen release would most likely be slower since hydrogen cannot be readily released to the liquid metal in contact with the fuel surface and since hydrogen solubility in He is infinite. How hydrogen would actually release from UZrH fuel in a liquid–metal-bonded fuel rod is unknown. Studies on this topic are required.

[3] Terrani points out that during a steady-state operation, the fuel surface is in compression while it is in tension at the central region of the fuel, and that during a reactivity insertion accident (RIA), a sudden fuel temperature increase actually lowers the stress across the fuel pellet [2]. Based on this information, the fuel pellet would seem to never crack. However, based on the assumed severe accident condition, after the cladding is destroyed, fuel pellets would fall to the bottom of the RPV. Pellets would break and cracks would form from the impact.

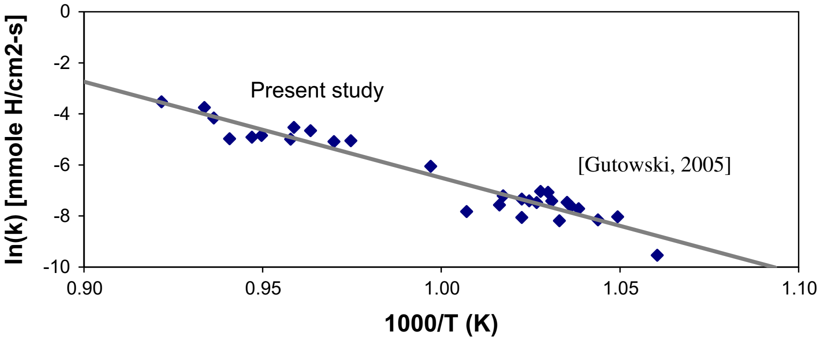

Fig. 8. Arrhenius plot of the absolute dehydriding rates and the linear trend line.

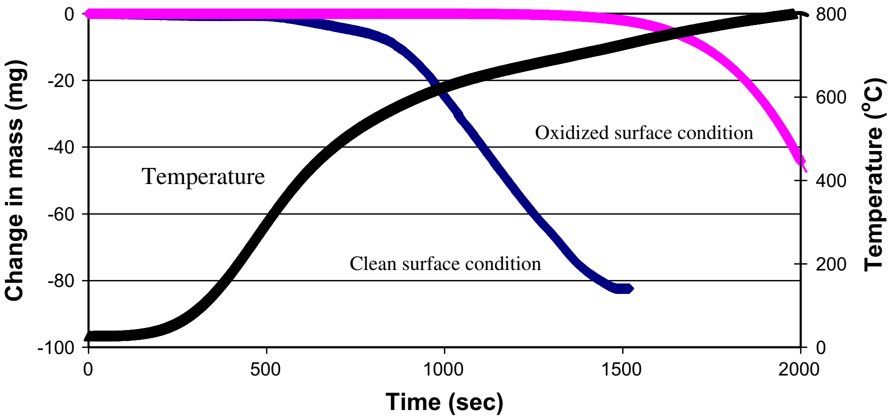

Fig. 9. Comparison of mass losses under oxidized and clean surface conditions.

depletion curve for the oxidized surface state shown in Fig. 9. In the figure, the mass loss for the clean surface condition and the temperature history reproduced from Fig. 6 are also included. Comparison between the two curves clearly shows that hydrogen release from clean surface specimens proceeds much faster than oxidized surface ones, correctly confirming the understanding that the native oxide layer acts as an effective diffusion barrier for hydrogen release. This would also imply that in real reactor fuel applications, effective prevention of hydrogen liberation from UZrH fuel under normal operations can be accomplished by intentionally forming a thick oxide layer on fuel pellet surfaces.

4. Conclusions

This paper discusses high-temperature absolute hydrogen desorption kinetics of zirconium hydride specimens with H/Zr ratio from 1.7 to 0 with no hydrogen backpressure for oxidized and clean fuel surface conditions. The temperature under study was in the range of 750–820 °C in order to create a hypothetical reactor accident condition manageable by the experimental setup. For the case of the clean surface state, hydrogen release was so rapid that most of the hydrogen had escaped from zirconium hydride specimen over the course of only 10 min in the temperature range of ~600–700 °C. During a postulated severe accident, the (at least initially) rapidly released hydrogen from newly-formed oxide-free surfaces and large cracks in fuel pellets could result in catastrophic damages the core internals and the RPV should an uncontrolled hydrogen explosion occur. For the case of the oxidized surface condition, the release rate was much slower due to the presence of the oxide layer, and was linear regardless of temperature and H/Zr ratio. This linear behavior cannot be explained by the conventional two process occurring in series: the solid-state diffusion of hydrogen in zirconium hydride to the free surface, and the recombination of hydrogen atoms at the fuel surface to form hydrogen gas. Nonetheless, the zeroth-order absolute dehydriding rate (k) was determined with an activation energy of 313 ± 17 kJ mol^{-1}. Following the postulated severe accident condition, when new surfaces and cracks become oxidized, hydrogen release would become slow. If the oxidation progresses quickly, the total quantity of liberated hydrogen gas would not be so large, possibly allowing the hydrogen igniters and recombiners to safely manage.

Acknowledgements

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