A. Sawatzky\textsuperscript{1} and C. E. Ells\textsuperscript{2}

Understanding Hydrogen in Zirconium


ABSTRACT: Selected examples of the Canadian contribution to the development of understanding of the behavior of hydrogen in zirconium alloys are reviewed. To solve the technical problems faced by the nuclear industry, it was necessary to have values for the solubility and diffusivity of hydrogen in the alloys, the diffusivity needed for the three gradients of concentration, temperature, and stress. With these quantities known, sensible models for the accumulation of hydrogen at points in the reactor components and the morphology of the resultant hydride phase were developed.

KEYWORDS: zirconium, hydrogen, zirconium hydride, Zr-2.5Nb, Zircaloy, diffusion, delayed hydride cracking

In accepting the Kroll award, we would like to use this medium to thank the committee for judging us as deserving of this high honor. We are very grateful. The committee noted that “one of its objectives is to collect first-hand accounts on key aspects of the history of the application of zirconium and its alloys” and went on to request from us a paper “outlining the pertinent aspects of the effects of hydrogen and hydrides on the structure and properties of zirconium-based alloys.” In attempting to meet the intent of the request, we have limited ourselves to some aspects of the Canadian contribution to the understanding of hydrogen (behavior) in zirconium alloys and, where it seems essential, putting this work in the context of the worldwide effort on the topic. In the space available in this publication, we can touch only on a few aspects of the vast literature on hydrogen in zirconium alloys. We deal largely with topics on which we ourselves worked, and in keeping with the Kroll tradition we are allowed to greatly over-emphasize our personal contributions. The dependence of the Canadian-designed CANDU on zirconium alloy tubes to provide the pressure containment places a particular urgency on avoiding any hydrogen/hydride-induced deterioration of the component. Thus, in this paper we concentrate on work devoted to the behavior of hydrogen in the pressure tubes.

The first Canadian power reactor conceptual design, NPD-1, had a steel pressure vessel, but the concept was changed to zirconium alloy pressure tubes in NPD-2 in 1957. The Canadian work on hydrogen in zirconium dates from that decision, although one of us, CEE, had worked previously on the topic. In the sections of text below we will generally describe the work in the chronological order of its being done; again, because of space constraints we can list only a few key references. We merely touch on the matter of mechanical properties and do not cover any aspects of the important topic of hydrogen ingress from water-

\textsuperscript{1} P.O. Box 137, Pinawa, Manitoba R0E 1L0, Canada.
\textsuperscript{2} P.O. Box 838, Deep River, Ontario K0J 1P0, Canada. (Tragically, Dr. Ells died in a car accident on November 30, 1999.)
side corrosion. We do not need to distinguish between hydrogen (protium) and deuterium and will list all concentrations of these isotopes in hydrogen equivalent.

**Terminal Solid Solubility**

The phase diagram of the Zr-H system has received an extraordinary amount of attention in several countries, as detailed in recent reviews [1-3]. From the viewpoint of the CANDU reactor, the $\alpha/\alpha +$ hydride phase boundary in the Zr-2.5Nb alloy (and to a lesser extent in Zircaloy-2, -4) is an item of overwhelming importance. This boundary is universally termed the TSS (for terminal solid solubility); when plotted as log hydrogen concentration versus reciprocal temperature, the boundary is generally linear. At the early stages of the CANDU development program it was speculated [4] that it might be acceptable to have hydrogen concentrations in the range 200 to 400 mg/kg present in the Zr alloy components at reactor operating temperatures, compared to the TSS at 300°C of about 70 mg/kg. However, with the advent of problems from delayed hydride cracking (DHC), the acceptable level has been reduced. Due to the large local volume expansion associated with hydride formation, it may be extremely difficult if not impossible to measure a true equilibrium value of TSS. In practice, the solubility line for precipitation during cooling, TSSP, is found at significantly lower temperatures than the line for dissolution during heating, TSSD. TSSP is dependent on the thermal history of the specimen prior to the start of cooling. The literature has often referred to the differences between TSSP and TSSD as a “hysteresis,” and contains various attempts to explain the source.

In 1957 Sawatzky, studying Zircaloy-2, made the first of the Canadian measurements of TSS [5]. His diffusion technique resulted in values of TSSP, and these were the reference values for AECL in the first half of the 1960s. Using a metallographic technique, Daniel [6] in 1965 found TSS(D) values in Zircaloy-2 somewhat lower than those in Ref 5, and at hydrogen concentrations below about 60 mg/kg his values were significantly higher than those predicted from the extrapolation of the higher concentrations, a result now discarded. In 1967 Kearns [7] at the Bettis Laboratory reviewed the bulk of the data on TSS(D) in zirconium, Zircaloy-2, and Zircaloy-4 available from the open literature; his estimate of the best fit of the data, often termed the “Kearns’ line,” has long been a standard to follow. Sawatzky and Wilkins [8] shortly afterwards measured TSSD in both Zircaloy-2 and Zr-2.5Nb, using a thermal diffusion technique. Their data were indistinguishable from the Kearns’ line. Sawatzky felt that the higher TSSP values were those of a metastable hydride phase. Coming to CRL in the early 1960s, Erickson continued [9] his pressure-temperature-composition measurements, attempting to find the reason for the hysteresis. While clearly establishing the existence of the hysteresis, and feeling that much of it was due to a metastable hydride phase, Erickson did start thinking about the effect of strain energy from hydride formation.

Following the DHC-related leaks in some of the pressure tubes at Pickering in 1974, there has been a succession of attempts to refine the measurement of the TSS values in zirconium alloys. In 1975 workers at WL, 3 particularly Ritchie, initiated experiments to make use of the Poynting effect, the internal friction spectrum, and the dependence of the elastic modulus on hydride concentration. Of the three techniques, the change in elastic modulus has proven most useful, clearly demonstrating the difference between TSSD and TSSP, and is still in use. Pan et al., in the most recent summary [10] of TSS in the Zr-2.5Nb alloy, have used

---

3 The laboratory at Pinawa, Manitoba will be listed as WL, the laboratory at Chalk River, Ontario as CRL, and that of Ontario Hydro in Toronto as OHRD.
the changes in elastic modulus as the primary experimental technique. Workers at WL found that metallography appeared useful for hydrogen concentrations as low as 8 mg/kg in pure zirconium, but was ineffective for Zr-2.5Nb. At CRL, Coleman and Ambler [11] used the onset of DHC to give an effective TSSD with data points close to the Kearns’ line. Differential scanning calorimetry, measuring the heat absorbed or evolved when hydrides dissolve or precipitate, was introduced by Tashiro at OHRD in the late 1980s, and has since been exploited by Khatamian and co-workers [12,13]. An essential component of the work on TSS is measurement of the hydrogen concentration in the sample. Although commercial equipment using hot vacuum extraction has been satisfactory, at CRL a HVEMS technique (hot vacuum extraction mass spectrometry) developed with many man-years of work [14] gives better accuracy in addition to distinguishing between the hydrogen isotopes.

Erickson and Hardie [15] seem to have been the first to address the effect of alloy additions on TSS. They reported on a range of alloys and found little difference in TSS between them. More recently it has been shown [16] that the alloy Excel, Zr-3.5Sn-0.3Mo-0.8Nb, does have TSS significantly higher than that of the other alloys studied. From all of the work thus far, the Kearns line and its linear extrapolation to lower concentrations, i.e., about 5 mg/kg, remains the standard for TSSD in zirconium, the Zircaloys, and Zr-2.5Nb. A recent summary of TSS values for Zr-2.5Nb as obtained by various techniques is presented in Fig. 1.

The various elastic and plastic stresses and strains caused in the hydride and surrounding lattice on hydride formation have a key role in both the hysteresis in TSS observed and in effects on TSS from externally applied stress. The Canadian work on this aspect is largely due to Puls, who started thinking about the problem(s) immediately following the first Pick-

![Graph showing values of TSS in Zr-2.5Nb obtained by different experimental techniques. Sources of the lines shown are: TSSD (a) calorimetry, (b) dynamic elastic modulus. TSSP: (c) calorimetry, (d) Slattery's data, (e) dynamic elastic modulus (TSSP2), (f) dynamic elastic modulus (TSSP1). The TSSP1 results from cooling from a higher temperature than used for TSSP2.](image-url)
ering leaks in 1974 and has continued the work to the present time. (To enable this work to be done, crystallographic relationships, not known in 1974, were required, and many of the gaps were filled by Carpenter and co-workers). A measurement of the partial molar volume of hydrogen in the alloys was made [17]. After Puls' preliminary work he elucidated the effects in a series of four papers [18-21], which now constitute the definitive explanation of hysteresis in metal hydrogen systems. Even a summary of his work on the topic is outside the scope of this paper.

**Diffusion**

*Isothermal Diffusion*

Because Zircaloy-2 was initially chosen for use as fuel cladding and pressure tube material in Canadian nuclear reactors, the diffusion of hydrogen in it was investigated over the temperature range 260 to 560°C [5]. Zircaloy-2 rods, with thin hydride layers on the surface, were heated at the desired temperature long enough to give a suitable hydrogen distribution. The mid-third of the specimen was then machined into seven layers and each analyzed for hydrogen by vacuum extraction. The diffusion coefficient was then obtained from the radial hydrogen distribution by the method described in Crank [22]. The results were in fair agreement with those of Mallett and Albrecht for zirconium [23].

The cold-worked Zr-2.5Nb used for pressure tubes (and some fuel cladding in the WR-1 reactor) as-fabricated has a microstructure consisting of α-grains elongated in the extrusion direction separated by a network of β-filaments. It was expected that the diffusivity of hydrogen would be higher in the β-phase than in the α-phase. The axial hydrogen diffusivity of this material was investigated over the temperature range 200 to 700°C [24]. In the method used, a rod of material was hydrided to somewhat less than TSS at the test temperature, butt welded to a similar unhydrided rod, and heated long enough to give a measurable hydrogen distribution. The diffusivity was then determined from the axial hydrogen distribution. The hydrogen diffusivity in Zr-2.5Nb was somewhat higher than in zirconium as observed by Kearns [25], who used the same experimental method. However, it was about 50 times higher in as-extruded Zr-20Nb, which is β-phase, than in zirconium. The experimental diffusivity in Zr-2.5Nb was much less than predicted using a simple mathematical model based on the microstructure. The high temperature used in hydriding the specimen and the diffusion anneal had changed the microstructure of the β-filaments. Skinner and Dutton [26], using a method in which tritium tracers were implanted over one surface of the specimen, were able to make diffusivity measurements in times short enough to avoid much change in the microstructure. Their experimental hydrogen diffusivities for as-extruded Zr-2.5Nb were in good agreement with predicted values.

*Thermal Diffusion*

High radial temperature gradients were thought to contribute to the hydride distribution seen in some defected Zircaloy-2 fuel cladding, so it was decided to investigate the thermal diffusion of hydrogen in this alloy [27]. The specimens used were hydrided Zircaloy-2 cylinders with constant temperature gradients along their axes. A typical result, obtained after a 34-day anneal, is shown in Fig. 2. The hydrogen concentration is plotted against temperature along the specimen and, as shown by the data points, there is a sharp cusp in hydrogen concentration at about 250°C. From the TSS curve, the region to the left of the discontinuity is α+δ-phase, and that to the right is α-phase. (Markowitz [28] also investigated
the thermal diffusion of hydrogen in zirconium using cylindrical geometry. He too observed a sharp change in hydrogen concentration at the $\alpha+\delta/\alpha$ interface, but it remained fairly constant over the $\alpha+\delta$ region. This was shown to be strictly because of the geometry.)

To explain the somewhat unexpected hydrogen distribution of Fig. 2, the differential equation giving the hydrogen flux as found in Denbigh [29] was used. Shewmon [30] had adapted the equation to the $\alpha+\delta$ region using the assumptions that: (a) hydrogen is the only element diffusing, (b) the hydride ($\delta$) is in equilibrium with the solid solution phase ($\alpha$) at every point, and (c) diffusion occurs predominantly in the $\alpha$-phase. The equation was solved for hydrogen flux and concentration in the $\alpha+\delta$ region for the case of the linear geometry used in the experiment. The theoretical hydrogen distribution, using known values for TSS, diffusion coefficient, and heat of transport, was calculated and is shown by the solid line in Fig. 2. The agreement is very good. The solid line in the $\alpha$-region is the steady state distribution under a temperature gradient and is also in good agreement with experiment. Sawatzky and Vogt [31] gave a more extensive mathematical treatment of the problem, taking account of the diffusion in the $\delta$-phase, movement of the $\alpha+\delta/\delta$ interface, variable temperature

FIG. 2—The thermal diffusion of hydrogen in Zircaloy-2.
gradient, and hydrogen pickup. Marino [32] developed a computer method based on the work of Sawatzky and Vogt that led to very good agreement with the experimental results in Fig. 2 as well as with Markowitz's results [28].

Several results may be obtained from Refs 27 and 31. At every point in the $\alpha+\delta$ region the hydrogen concentration increases continuously, and there is a hydrogen flux toward the colder region. If the hydrogen diffuses in the $\alpha$-phase, the flux is determined by the temperature gradient and the TSS gradient. The hydrogen flux at the cold surface leads to the formation of a hydride layer at this point. The movement of the $\alpha+\delta/\alpha$ interface is of interest. For the experimental hydrogen distribution in Fig. 2, the hydrogen flux toward the $\alpha+\delta/\alpha$ interface is less than away from it and the interface moves toward the colder end. On the other hand, if the hydrogen pickup at the hot end leads to a hydrogen distribution in the $\alpha$-region such that the concentration gradient at the interface is the same as that of the TSS curve, as given by Curve A, the interface position remains fixed. For higher pickup rates, the interface moves toward higher temperatures. In fact, for high enough pickup rates, the interface may be at the hot surface, in which case a solid hydride layer will form at both hot and cold surfaces with an $\alpha+\delta$ region in between. This result has been observed in defected fuel cladding.

Hydride Orientation

Workers in zirconium metallurgy over the past two decades may not realize the extensive concern felt in the 1960s on the matter of hydride orientation and stress orientation of hydrides. Although it was well known that hydrides could have deleterious effects on ductility parameters, Marshall and Louthan [33] showed that with the normals to the hydride platelets parallel to a tensile stress the tensile ductility could be reduced to negligible values at room temperature from a hydrogen concentration as small as 40 mg/kg. (Although Ref 33 is dated 1963, the information was released via progress reports in 1961.) This result had worldwide implications for the use of zirconium alloy structural components. Each of the countries—United States, United Kingdom, Japan, Sweden, and Germany—had significant roles in establishing the fabrication procedures that largely eliminated any tensile failures from oriented hydrides in reactor components. Nevertheless, Schemel wrote [34] "The work at Atomic Energy of Canada Ltd. (AECL) provided much of the technical data on which the commercial use of zirconium was based."

The first CRL work on directional precipitation of hydrides in Zircaloy-2 was completed in 1962 [35], demonstrating that the hydride platelet normals tended to form in directions perpendicular to the direction of prior strain of the specimen. CRL staff then worked with Wah Chang, of Albany, Oregon, to develop a fabrication route for rolled plate up to 50 mm thick in which the subsequent hydride platelets had normals in the thickness direction of the sheet [36]. This material gave much more satisfactory specimens than did either of the thin-walled tubes, thin sheet, or rod previously used. Evans and Parry [36] studied the interrelation between hydride orientation, hydrogen concentration, and test temperature on tensile ductility. When the test temperature reached 300°C, the ductility was independent of hydride orientation. Parry went on to study stress or stress-induced orientation in both Zr-2.5Nb-0.5Cu [37] and Zr-2.5Nb [38]. Price [39] and then Bell and Duncan [40] were to make further contributions to knowledge on the Zr-2.5Nb alloy. Some years later Cheadle et al. [41] were to refine the stress orientation measurements on tubes, using specimens that avoided the flattening used in many previous studies.

Ells [42] in 1968 reviewed all of the open literature information on orientation and stress orientation of hydrides in the zirconium alloys. By that time there was sufficient information to relate hydride orientation to fabrication procedure with considerable confidence. The basic
mechanisms of stress reorientation remained unknown, but shortly Ells [43] showed that an extension of a treatment by Li [44] provided at least a qualitative explanation of the experimental observations. Two decades later, Puls [45], making use of the advances in understanding he had developed in the interaction between hydrides and stress, put the explanation on a more satisfactory basis.

Zirconium Alloys in an Organic-Cooled Reactor

The Feasibility of Using Zirconium

It was decided, in the late 1950s, that Canada would build an experimental organic-cooled nuclear reactor (WR-1) using natural uranium oxide or carbide as fuel. The use of organic coolant allowed a higher temperature than heavy water at equivalent or lower pressures, with the target temperature of 400 versus 300°C for heavy water giving a higher thermodynamic efficiency. The use of natural uranium fuel precluded the use of steel for pressure tube or fuel cladding material. A sintered aluminum material (SAP) and beryllium were considered for this purpose, but both were very brittle. The possibility of cladding zirconium with a thin metal layer was considered, but the only feasible metal was aluminum and no method of readily applying it was found. The Americans had looked into using unclad zirconium alloys, but found they hydrided very rapidly at 400°C in organics such as Santowax OM [46–48]. However, Shannon [49] had shown that adding small amounts of water vapor to hydrogen gas reduced the hydriding rate at 400°C by several orders of magnitude. He attributed this to water molecules taking up the sites on the zirconium oxide onto which otherwise the hydrogen molecules would be absorbed. It seemed worthwhile to see whether water would have the same effect of reducing the hydriding rate of zirconium in organics (Santowax OM and HB-40). In fact, Troutner [50] had obtained a lower-than-expected hydriding rate in organics in at least one of his tests, which was thought possibly due to water in the organic. An organic loop (X-7) in the NRX reactor at CRL enabled testing both in and out of reactor. Unclad Zircaloy-2 in this loop picked up hydrogen at 400°C at a rate several orders of magnitude less than in unreplenished autoclaves at Canadian Westinghouse operating at the same temperature. It seemed that the water in the organic coolant in the X-7 loop was enough to provide protection against hydriding. When the water level in the autoclaves was maintained at about 100 mg/kg, the hydriding rate was also decreased by several orders of magnitude. The preliminary results showed that it might be possible to use zirconium alloys in organic-cooled reactors. The early tests on zirconium in organics were carried out mainly at CRL in 1961–63, described by Sawatzky [51]. The work on hydrogen pickup by zirconium alloys in organics after 1963 was done at WL. It resulted in Zr-2.5Nb and Ohzhennite 0.5 becoming the alloys of choice for use in organic-cooled reactors. This work is reported by Boulton [52].

Hydrogen Sinks in Zirconium Components

The heavy water moderator in the WR-1 reactor was contained in a tank, the calandria, which had a lattice of vertical aluminum calandria tubes through which the pressure tubes passed. CO₂ flowing down the annulus between the two tubes served as thermal insulation. The temperature drop across the gas annulus was about 300°C. If the pressure tubes were of zirconium, it was thought that zirconium fins, welded to the outside of the pressure tubes, might be exposed to a sufficient temperature gradient to serve as hydrogen sinks, thereby increasing the pressure tube life. Wilkins and Sawatzky [53] demonstrated in an out-reactor
test that the hydrogen concentration in the pressure tube could be maintained at well below TSS for many years.

A practical demonstration that thermal diffusion can be used to protect load-bearing reactor components against hydrogen embrittlement arose by accident [54]. The conventional fuel elements in WR-1 consisted of UC or UO$_2$ pellets in zirconium alloy tubular sheaths with zirconium wire-wrap spacers spot-welded to the outside. A gas plenum about 1 cm long at the upper end of each element maintained the fission gas pressure at acceptable levels. Several fuel elements without the wire wrap were found to have defected over the plenum as a result of heavy hydriding, after 200 days in the reactor at a sheath temperature of 450 to 500°C. The sheath over the plenum was 100 to 150°C colder than over the fuel, and most of the hydrogen picked up by the sheath for a distance of about 7 cm along the fuel pellets had diffused to the plenum, whereas the rest of the sheath was heavily hydrided. A mathematical model gave a hydrogen distribution along the sheath in excellent agreement with that observed. The wire wrap in the conventional fuel elements, being colder than the sheath, was heavily hydrided, leaving the sheath itself hydride-free at the operating temperature, thereby serving as a hydrogen sink.

Hydrogen Distribution in Fuel Channels

Joints in the WR-1 Reactor

The pressure tubes in the WR-1 reactor were fabricated from zirconium alloys, preoxidized, and mechanically connected to the out-of-core steel piping by sandwich-type steel joints, Fig. 3a. Since steel is fairly permeable to hydrogen, two pressure tubes were removed from the reactor in 1971 after about 3000 h of operation at 350°C, and the joints checked for hydriding. The lower joint had picked up about 80 mg/kg, but the upper joint had picked up about ten times this amount. An analysis of the hydrogen distribution suggested that in
the lower joint most of the hydrogen had entered by Route 2, Fig. 3a, whereas in the upper joint a considerable amount of hydrogen had also entered from the CO₂ annulus, Route 5. The hydrogen probably entered the annulus through the steel extensions, Route 4. Because of a 300°C temperature drop across the annulus, the pressure tube may have acted as a gas separation tube [55], leading to a higher hydrogen concentration over the upper joint than over the lower one.

A duplicate of the pressure tube annulus system was set up in the out-reactor arm of a WR-1 organic loop and operated under in-reactor conditions except for the neutron flux. The annulus had gas sampling positions every 40 cm. The CO₂ in the reactor annuli flowed downward at about 400 mm/min, and at this flow rate the hydrogen concentration over the upper joint was about 10% by volume and 0.03% over the lower joint. A mathematical analysis of the situation suggested that downflow of the gas tended to allow the hydrogen concentration to build up, whereas reversing the flow would permit the hydrogen to be swept out. The gas flow direction was reversed and the same flow rate led to hydrogen concentrations of 0.1 and 0.03% over the upper and lower joints, respectively. The hydriding of the upper joint from the annulus could therefore be largely eliminated by having the CO₂ flow upward rather than downward. Two other approaches to reduce hydriding under the joint were considered: (a) bare zirconium wire embedded in the joint or (b) zirconium fins seam welded to the outside of the tube inboard of the joint to serve as a hydrogen sink. Either of the approaches probably would have been effective, but work on the organic-cooled reactor was stopped to allow concentration on the heavy water-cooled CANDU.

**Joints in the Pickering-3 Reactor**

The Zr-2.5Nb pressure tubes in Pickering-3 had been pre-oxidized to reduce deuteriding. The DHC cracks in the tubes in which leaks were first observed near the rolled joints in 1974 may have been initiated before reactor startup. Incorrect rolling procedures led to high tensile residual stresses, and the hydrogen concentration in the as-installed tubes was sufficient to cause delayed hydride cracking during cold shutdowns. However, enhanced deuterium concentrations found in the joints [56] raised the possibility of the hydrogen equivalent becoming sufficiently large at later times for DHC to occur at operating temperatures. The possible routes by which deuterium might enter the zirconium in the joints are shown in Fig. 3. To get a better understanding of the hydriding mechanism, a number of joints were rolled onto short lengths of pre-oxidized Zr-2.5Nb tubes and placed in an out-reactor hot water loop at operating conditions. At regular time intervals a joint would be removed and the hydrogen distribution determined. A mathematical analysis indicated that the hydrogen entered the tube fairly uniformly over the joint, at a rate decreasing with time. The outer surface of the tubes showed regions where there was little oxide. An unexposed joint was cut up and much of the oxide on the outer surface found to be missing, probably damaged during rolling. The leakage of minute quantities of water along the steel/zirconium alloy interface apparently slowly repaired the oxide layer. These results suggest that Route 2 is the main avenue for hydriding. The rolled joint cracking problem has been largely solved by changing rolling practices to keep the residual stresses low. In addition, programs have tested modified joint designs to reduce the deuteriding rate. These include longer joints to increase the path length for deuterium diffusion, deuterium barriers such as chromium, the use of getters such as yttrium, and fins as originally proposed for the pressure tubes in the organic-cooled reactor. The getter concept was developed to a prototype so that it could be considered for use in future CANDU reactors.
Hydride Blisters

The fuel channels in the CANDU reactors are horizontal, with the pressure tubes kept from touching the calandria tubes with garter spring spacers. The rupture of a Zircaloy-2 pressure tube in Pickering NGS-2 in 1983 was due to movement of the garter springs, allowing the pressure tube to contact the cooler calandria tube. A row of hydride blisters had formed at the points of contact and had been instrumental in initiating the crack that followed the row of blisters. The blisters formed at the cold spots from thermal diffusion. Using thermal diffusion theory, methods were developed for determining the size of a blister as a function of time [57]. The corrective measures taken for current and future CANDUs are described in detail in Ref 58.

Hydride blisters had been observed on a Zr-2.5Nb pressure tube removed from the WR-1 reactor in 1977, but their significance had not been realized until the 1983 incident [59]. Four blisters, axially aligned, up to 1 cm in diameter and almost through-wall, were found in this WR-1 tube, which had been in-reactor for 34,874 operating hours. The tube had been monitored for radiation-induced elongation and had been elongating at a constant rate when this seemed to stop suddenly. The moving end of the pressure tube apparently jammed against restraining straps, resulting in bowing and eventual contact with the colder calandria tube. After a further 6000 h of operation the pressure tube was removed from the reactor. The time required for growth of the largest blister was calculated to be 6770 h. This was in reasonable agreement with the 6000 h of estimated contact between calandria and pressure tubes and gave confidence in the method used for calculating blister growth. The OHRD staff have made a large contribution to the understanding of blister growth, and then to its prevention.

Delayed Hydride Cracking

The matter of DHC in CANDU pressure tubes has involved a large continuing effort in Canada in the period since 1974. Major players in the study have been CRL, WL, and OHRD, with other work in Canada being undertaken at the Universities of Toronto, Alberta, Windsor, and New Brunswick. The three major players also jointly or individually employed various consultants from time to time, E. Smith deserving of special note. Other countries have contributed to the understanding of DHC, but the major proportion of the work has been done in Canada. It would be ridiculous to close this paper without mention of DHC, but at the same time impossible to do other than touch on some of the highlights of the work.

The principal characteristics of the DHC in the Zr-2.5Nb have been well established. Hydrogen diffuses to regions of high tensile stress at a crack tip and forms hydride there, eventually resulting in an increment of crack growth, and the process repeats at the new crack tip. The dependence of crack velocity on the stress intensity factor is shown schematically in Fig. 4. There is a sharp threshold \( K_{th} \) in Stage I) for crack initiation at a stress intensity factor, typically 5 to 10 MPa\(\sqrt{m} \), followed by a range in which the crack velocity is fairly independent of the stress intensity factor value (Stage II), but eventually the fracture toughness of the metal matrix is exceeded (Stage III). In the early experiments the velocity in Stage II was shown to increase exponentially with temperature, typically reaching \( 10^{-6} \) m/s at 300°C. Later it was shown that at temperatures above some value the crack growth rate was much higher on cool down to test temperature compared to heat up to the same temperature, which explained some of the large variability observed in the very early results. The current understanding of dependence on thermal history is illustrated in Fig. 5. From
the viewpoint of integrity of reactor components, particularly pressure tubes, the value of the stress intensity factor was disconcertingly low and the crack growth rates disconcertingly high; it was essential to learn how to minimize the hazard. The understanding of DHC fell into two issues: (a) how the crack initiated, and (b) the accumulation of hydrogen at the crack tip that resulted in the crack growth. Here we are concerned only with the DHC mechanism as such and not with the applications of the theory to repair, operate, or construction of reactor components.

The first recorded observation of DHC in zirconium alloys is probably that of Weinstein and Holtz [60], working on a contract sponsored jointly by AECL and the USAEC, although they acknowledged some unpublished work by Ostberg. They noted in their summary, “... Zr-2.5Nb ... is susceptible to hydrogen-induced delayed failure.” The observations were for specimens containing 500 mg/kg of hydrogen stressed to 275 MPa, and at the time the result did not seem to be of concern to the pressure tubes, whose hydrogen concentration would be an order of magnitude less and operating at half the stress. Later, in 1971, Aitchison certainly demonstrated DHC in the high-strength zirconium alloy Excel, although it was not recognized as such at the time and the observation was only recorded in internal progress reports. Also in 1971, Stevens and Dutton [61] issued an important document on the motion of hydrogen in combined gradients of temperature and stress. They defined a new quantity, \( V^* \), the volume of transport, in analogy with \( Q^* \), the heat of transport. They left the equations

![Diagram](image1)

**FIG. 4**—Schematic form of the relationship between stress intensity factor and DHC velocity.

![Diagram](image2)

**FIG. 5**—The dependence of DHC velocity on the temperature of approach. Arrows on the curves show the difference between heating and cooling cycles. A full explanation of these effects is provided in Ref 79.
in terms of the flux of hydrogen in the gradients. Using the mathematical technique used by Sawatzky [27] for the thermal gradient (with stress constant), Ells and Simpson [62] made the first attempt to integrate the flux equation to obtain the rate of hydrogen (hydride) buildup at a region of high tensile stress (at constant temperature). Following Aitchison's work, the next observation of DHC in zirconium alloys was in some welded end caps of Zr-2.5Nb fuel sheathing, the experimental work being done by Simpson, Aldridge, and Ambler. The work by Aldridge and Ambler was not written for the open literature, but the Simpson work was published [63] with Ells as a co-author. Aldridge and Ambler were the first to recognize this failure as DHC and postulated the correct mechanism, essentially as described above. They solved the technical problem for the fuel sheathing merely by stress relief of the weld, and DHC might have merited little further work were it not for the failure of the tubes in Pickering in August 1974 and concerns for other reactors.

During the autumn of 1974 each of CRL, WL, and OHRD had initiated experimental programs to define the parameters of DHC in the cold-worked Zr-2.5Nb alloy (and shortly the Hitachi laboratory in Japan started similar work on heat-treated Zr-2.5Nb). The early published work was done using notched tensile-type specimens and then obtaining crack extension by optical examination [64–66] or measuring time to failure [67]. Better methods of detecting crack growth were developed, acoustic emission [68,69] at CRL and potential drop [70] at WL, along with the use of cantilever beam and compact tension specimens. Apart from the large number of measurements of $K_\text{eff}$ and crack velocity, various specialized experiments were undertaken. Coleman [71] showed that the crack velocity increased with increasing percentages of basal plane normals parallel to the stress direction. At WL, it was demonstrated that stringers of β-phase in the direction of crack growth increased the growth rate [26] attributed to the higher diffusivity of hydrogen on the β-phase compared to the α-phase. Ells et al. [72] showed that a tensile stress aligned parallel with the normals to the hydride platelets increased the time required for hydride dissolution at a range of temperatures; quantitative information on this topic was desired when thinking of how quickly the hydride present at crack tips at low temperatures would be eliminated as the pressure tube went to operating temperatures.

Coincident with the initiation of the experimental programs, in late 1974 Dutton and Puls started an intensive study on the matter of diffusion of hydrogen to the crack tip and by mid-1975 had achieved a sophisticated crack growth equation [73], which gave semi-quantitative agreement with the experimental data for Zr-2.5Nb. The concept of volume transport was discarded. Lee-Whiting [74] over the same period developed corresponding equations, but with more emphasis on the form of the stress field near the crack tip. In this stage of the theory, transformation from hydride volume to crack growth required an assumption of hydride thickness. Then workers at WL, particularly Puls, but with contributions from other colleagues, continued to fine-tune the equation and collect the data to test it. First the discontinuous nature of the cracking was included [75]. By late 1977 considerably more data on growth rates were available, and they developed a model [76] to differentiate between the Stage I and Stage II growth. Late in 1978 they had started to include refinements from the elastic strain energies at the hydrides, and several years later wrote out a final growth rate equation [77]. With the elastic strain energies included in the theory, Ambler [78] was able to explain the dependence of velocity on direction of approach to test temperature. The current up-to-date review on the theory of crack velocity is that of Shi and Puls [79]. The differences in crack velocity between different alloys and the effect of material strength is not yet completely understood. The extreme example encountered thus far is the factor of 10 higher rate in Excel alloy compared to Zr-2.5Nb [80]. The more important matter is the effect of irradiation on the rate in Zr-2.5Nb, studied in detail at CRL and WL [81]. In general the rate is increased by irradiation by factors of up to 5, but the increase is a function
of starting material, irradiation temperature, increase in yield strength due to irradiation, and changes in the amount and morphology of the β-phase. The theory does not yet give a satisfactory quantitative model including all of these variables.

The crack initiation process has been much more difficult to model than the crack growth. After 23 years of study it is felt that three situations must be considered: (a) a sharp crack for which a threshold stress intensity factor $K_{th}$ can be defined, Fig. 4, (b) a shallow smooth notch to be characterized by the maximum normal stress, and (c) a nominally smooth surface for which the surface tensile stress causes the crack initiation. In one of the earliest studies, Nuttall [65] did not find a value of $K_{th}$, but Coleman [67] soon found a value of about 5 MPa\(\sqrt{m}\) for Zr-2.5Nb at 170°C, using notched tension specimens. Coleman and Ambler [68] were to continue the work using acoustic emission with cantilever beam specimens. Cheadle was to be a leader in measurements of crack initiation on nominally smooth surfaces and surfaces with small artificial defects. In part of this work, Cheadle and Ells [82] studied initiation in both cantilever beam specimens and internally pressurized lengths of a full-size pressure tube. One problem in assembly of the data on crack initiation arose from the difficulty in deciding if or not there was a small crack in the hydride at a pre-machined notch. A further problem came from the effect of thermal cycling to effect or generally reduce the value of $K_{th}$ observed [83], thus greatly increasing the number of variables to be considered. In the study of nominally smooth surfaces there was the difficulty of characterization of the defects and the coincident needed to present results in terms of probability of failure in a given time for a given calculated surface stress. A large volume of data was assembled on these matters.

The mechanistic goals was the same as that for crack velocity, viz., obtain an understanding of crack initiation in terms of basic properties of the material(s), but there are far fewer publications on this topic than on crack growth. The later fracture work at WL is reported in a series of papers having Puls as author or co-author [84–90]. Based on this work, and a large series of tests undertaken by Sagat, a satisfactory model for crack initiation at sharp crack tips and shallow notches has been developed by Puls, Shi, and Sagat. Any description of the model is beyond the scope of this paper.

Conclusions

In the four decades since the decision to use zirconium alloy pressure tubes in the CANDU reactor, a large quantity of knowledge on the behavior of hydrogen in the alloys has been generated. The authors were privileged to be able to contribute to this knowledge and regret that in the limited space available for this paper it has not been possible to acknowledge the individual contributions from all of those involved.

References


Copyright by ASTM Int'l (all rights reserved); Sun Mar  6 23:27:34 EST 2011
Downloaded/printed by
Arthur Moses Thompson Motta (Pennsylvania State Univ) pursuant to License Agreement. No further reproductions authorized.


[37] Parry, G. W., “Strain Induced Directionality of Zirconium Hydride Precipitates in Zirconium-2.5wt% Niobium-0.5wt% Copper Alloy,” AECL-1888, 1963.
[40] Bell, L. G. and Duncan, R. G., “Hydride Orientation in Zr-2.5%Nb; How it is Affected by Stress, Temperature and Heat Treatment,” AECL-5110, 1975.


