Evaluating the Risk of Delayed Hydride Cracking in Components Made from Zirconium Alloys

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Abstract
One of the products of corrosion of components made from zirconium alloys is hydrogen, some fraction of which is absorbed by the component. The solubility limits for hydrogen are very low in the usual range of operating temperatures, and as a result, hydrides are often present in components. These hydrides are brittle and carry the potential for cracking. This cracking appears as a loss in toughness or can be time dependent. The latter is called delayed hydride cracking (DHC). DHC has several limits associated with hydrogen concentration, applied stress intensity factor and temperature history. Safe and trouble-free operation of components may be achieved by staying within these limits. In this paper the limits are outlined and methods of assessment to avoid failure are outlined based on answering seven questions:

1. Is the material susceptible to DHC?
2. Is sufficient hydrogen present to form hydrides at a crack tip?
3. Was the temperature history conducive to DHC?
4. Were any temperature gradients present?
5. Are any sharp flaws present and, if so, how large are they?
6. Are large tensile stresses present?
7. Is the combination of 5) and 6) sufficient to exceed $K_{\text{IH}}$, the limit for cracking?

Keywords
- zirconium alloys
- delayed hydride cracking
- hydrogen concentration
- temperature history
- limits for cracking

Introduction
Oxidation during corrosion of zirconium alloys in water reactors does not present a problem for structural components with thick walls. Oxides grow slowly and represent a small reduction in cross-section that can be easily accommodated by design. For example, in a Zr-2.5Nb alloy pressure tube in a CANDU nuclear reactor the maximum oxide thickness after 14 years operation in water at 295°C...
(563°F) is 25 µm, which reduces the tube wall by less than 0.5%. The other product of the corrosion in water is hydrogen through:

$$\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 4\text{H}.$$  

Some fraction of the hydrogen is absorbed by the component. When the terminal solid solubility (TSS) limit for hydrogen in zirconium is exceeded, hydrides are present. The solubility limit has an apparent hysteresis with temperature; for a given hydrogen concentration, hydrides dissolve (TSSD) at a higher temperature on heating than when hydrides precipitate (TSSP) on cooling, Figure 1.

The maximum initial amount of hydrogen allowed by the ASTM standard for nuclear components is 25 ppm by weight. The solubility limits for hydrogen are very low in the usual range of operating temperatures — up to 350ºC (662ºF). Hydrides are always present at room temperature, and could be present on heating up to 225ºC (437ºF) and will precipitate at 175ºC (347ºF) on cooling. Hydrides precipitate as platelets; they are brittle and may crack. This cracking appears as a loss in toughness or may be time dependent. These time-dependent phenomena arise because the hydrogen in solution can move in gradients of hydrogen concentration, temperature and stress. The last gradient leads to a process called delayed hydride cracking (DHC). DHC has been responsible for cracks in nuclear reactors and in chemical plants, thus we need to understand the limits of the process so safe and trouble-free operation may be achieved by staying within these limits.

Evaluation of failed components, experiments on specimens and theory have quantitatively demonstrated the limits associated with hydrogen concentration, temperature history, stress and stress intensity factor, $K_I$. In this paper we outline the basic mechanism for DHC, describe the limits and apply them to assess how to avoid two examples of failures.

**Basic Mechanism of Delayed Hydride Cracking**

Consider a zirconium-alloy component containing a flaw and some hydrogen. If there is stress at the flaw, hydrogen will flow from the unstressed region to the flaw according to the Nernst-Einstein equation, which can be written for this application as shown in Equation 1, where $J$ is the hydrogen flux, $D$ the hydrogen diffusivity, $C$ the hydrogen concentration in solution, which is assumed to be dilute, $R$ is the Gas Constant (8.314 kJ/mol.K), $T$ is the temperature in K, $V_H$ is the partial-molal volume of hydrogen in zirconium, and $\sigma$ is the hydrostatic stress.

$$J = -D\left(V_C + \frac{CV}{RT}\right)$$  

**Equation 1. Hydrogen flux.**

$$\nu = \nu [C_s - C_p \exp (\sigma_s V_H / RT)]$$  

**Equation 2. Crack velocity with apparent activation energy.**

$$\nu = \nu \exp (-Q/RT)$$  

**Equation 3. Crack velocity.**

Initially if the hydrogen concentration in solution is everywhere the same (i.e., the gradient $\partial C/\partial x = 0$) then hydrogen will tend to flow because of the stress gradient toward a flaw under tension (i.e., $J > 0$), and the hydrogen concentration at the flaw will increase until equilibrium is reached and the flux of hydrogen goes to zero. Under these conditions the movement of hydrogen is opposed by the hydrogen concentration gradient, which grows more and more negative with time, and finally becomes equal to the stress-gradient term in Equation 1 at equilibrium, and $J = 0$.

However, cracking is not an equilibrium process. If sufficient hydrogen accumulates at the flaw tip to exceed the TSSP concentration, $C_p$, hydrides form. In this instance, equilibrium cannot be attained and steady state ensues.

**Figure 1.** Solubility limit for hydrogen in Zr-2.5Nb, TSSP, determined by cooling, and hydrogen concentration in solution when hydrides are present, TSSD, determined by heating, showing low values below 200ºC (392ºF) and an apparent large thermal hysteresis between heating and cooling.
At the flaw tip, the hydrogen concentration is fixed at $C_P$ and the steady-state hydrogen flux continually provides hydrogen that precipitates as hydride. With time the hydride grows and, if the tensile stress is large enough, the hydride cracks and the flaw extends by the length of the hydride. These steps are then repeated to grow the crack. Since cracking of the hydride is a rapid process, the rate of growth of the hydride and its subsequent cracking are controlled by the diffusion of hydrogen into the flaw-tip region. The diffusion takes time and thus the cracking is delayed, hence the name delayed hydride cracking.

A simple formula for the crack velocity, $v_c$, can be derived from Equation 1 with the assumption that the steady-state flux of hydrogen to the flaw is controlling the process,[5] as shown in Equation 2, where $W \approx \text{constant} \times D$, $C_b$ = concentration of hydrogen in solution in the bulk material and $\sigma_y = -2.4 \times$ yield strength, for plane strain.

### Limits of Hydride Cracking

Hydrides are required for cracking. At a particular temperature a critical hydrogen concentration, $C_{crit}$, is required in solution in the metal matrix so that the flow of hydrogen to the flaw tip is sufficient to form a hydride. The value of $C_{crit}$ represents Limit # 1. Note that hydrides are not required to be present in the metal matrix for DHC. Once hydrides are present in the metal matrix, the crack growth rate is independent of hydrogen concentration. Figure 2 provides an example showing the critical hydrogen concentration for DHC to start and its independence once TSSP in the metal matrix is exceeded.

The temperature dependence of cracking is complicated,[7] Figure 3, although much of the literature on DHC describes crack velocities phenomenologically with Arrhenius equations, as shown in Equation 3, where $v_c = \text{constant}$ and $Q = \text{an apparent activation energy}$.

As the temperature is raised from $T_1$, cracking velocity follows Equation 3 until a temperature is reached where the cracking rate starts to decline, $T_2$, and eventually stops at a slightly higher temperature, $T_3$, even if hydrides are present in the component; $v_{\text{min}}$ goes to zero in Figure 3. This temperature represents Limit #2 for DHC. $T_3$ depends on $T_1$; when $T_1$ is

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**Figure 2.** Crack growth rate in Zr-2.5Nb at 182°C (360°F), showing a limit of DHC based on hydrogen concentration, $C_C$. The experimental results are from Kim[6] and the theory is determined using experimentally measured properties of Zr-2.5Nb[5] in Equation 2.

**Figure 3.** Temperature dependence of DHC growth rate in zirconium alloys showing the effect of heating and cooling to the test temperature[7].
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Figure 4. Crack growth rate after cooling in Zr-2.5Nb containing two hydrogen concentrations. $T_6$ at the maximum crack growth rate is attained at TSSP. The experimental results are from Cirimello et al.\cite{10} and the theory is based on Equation 2.

Figure 5. Dependence of crack growth rate on $K_I$ showing a threshold, $K_{IH}$, below which cracks do not grow, a region where the crack growth is stable and its rate is usually independent of $K_I$, and eventual rupture when $K_{IC}$ is exceeded with a long unstable crack.

25°C (77°F), $T_1$ is about 210°C (410°F)\cite{8}, but when $T_1$ is 230°C (446°F), $T_3$ is raised to 260°C (500°F)\cite{9}. This phenomenon arises because at a certain temperature the yield strength has decreased to the point where there is no longer a flux of hydrogen to the flaw tip, and cracking stops. On cooling from some high temperature, $T_e$, a temperature is reached where cracking starts, $T_3$; this temperature is equivalent to Limit #1 based on hydrogen concentration. Again, the material can crack even if all the hydrogen is in solid solution and no hydrides are present in the bulk of the component. With additional cooling, the velocity reaches a maximum value at $T_4$, which coincides with TSSP. Cracking at subsequent lower temperatures again follows Equation 3, Figure 4.

A threshold mechanical loading is required to fracture a hydride and thereby initiate cracking. If no flaw is present, the process can only start with very large tensile stresses; if a sharp flaw is present in the component, a threshold stress intensity factor, called $K_{IH}$, has to be exceeded. $K_{IH}$ represents Limit #3 for DHC. Once a crack has been initiated, its growth rate will have little dependence on crack length, and therefore $K_{IC}$, because the stress distribution, and therefore stress gradient, at the crack tip stays approximately constant as the crack grows. Figure 5 describes this behavior. The value of $K_{IH}$ can vary but a reference lower bound is 4.5 MPa√m\cite{10}. $K_{IH}$ has little temperature dependence up to about 300°C (572°F), but increases rapidly at higher temperatures\cite{11}, Figure 6. The consequence of this increase in $K_{IH}$ is that at some high temperature, $T_0$, the crack growth rate declines to zero, Figure 6, representing Limit #4.

Another potent way to move hydrogen is down a temperature gradient. At equilibrium with no temperature gradient, in a piece of zirconium containing hydrogen in solution, the hydrogen atoms jump in all directions at the same rate and the concentration of hydrogen remains constant throughout the piece. The jump frequency of hydrogen atoms is greater in hot material than in cold material. If these two materials are joined and allowed to reach equilibrium without forming hydrides, the number of atoms jumping from the cold region to the hot region per unit time must be equal to the number of atoms jumping from the hot region to the cold region. To satisfy this condition, the concentration of hydrogen atoms must be higher in the cold region than in the...
hot region. Thus a concentration gradient is set up at equilibrium with a greater concentration of hydrogen in the cold region than in the hot region. The equilibrium is often characterized by the heat of transport, which is evaluated from observations of hydrogen concentrations in solution in materials with a known temperature gradient \([12]\). If the temperature of the cold region is below TSSP, hydrides will form. Unfortunately, practical demonstrations of temperature gradients are hydride blisters in pressure tubes in contact with calandria tubes \([13]\) and hydride layers on the outside surface of PWR fuel cladding at high heat fluxes \([14]\). In DHC, if a flaw is cooler than its surrounding material, the temperature gradient will reinforce the effects of the stress gradient leading to faster crack growth and higher values of \(T_3\) \([15]\). For example, a temperature gradient of 20\(^\circ\)C/mm (68\(^\circ\)F/mm) increases the crack growth rate by a factor of about 2.5 and raises \(T_3\) by about 150\(^\circ\)C (302\(^\circ\)F).

In summary, delayed hydride cracking is driven by a gradient in stress that can be reinforced by a temperature gradient. Four limits have been identified:

1. Sufficient hydrogen in solution in the bulk is required to form hydrides at a stressed crack tip — this limit is characterized by \(C_C\) at a constant temperature or \(T_5\) at a constant hydrogen concentration.
2. On heating a temperature is reached where the flux of hydrogen to the flaw tip is insufficient to form a hydride — this limit is characterized by \(T_3\).
3. A threshold stress is required to crack a hydride at the flaw tip — this limit is characterized by \(K_{IH}\).
4. Zirconium alloys are immune from DHC above an upper temperature called \(T_0\).

Answering Seven Questions to Avoid Cracking

To discover the potential for failure in a component, or understand a failure so it can be avoided in the future, one needs to evaluate the margins on the limits for DHC and answer seven questions:

1. Is the material susceptible to DHC?
2. Is sufficient hydrogen present to form hydrides at a crack tip?
3. Was the temperature history conducive to DHC?
4. Were any temperature gradients present?
5. Are any sharp flaws present and, if so, how large are they?
6. Are large tensile stresses present?
7. Is the combination of 5) and 6) sufficient to exceed \(K_{IH}\), the limit for cracking?

Two examples will be discussed to illustrate the principles.

WELDING ZR-2.5NB

The first practical example of DHC was found in experimental fuel cladding made from Zr-2.5Nb. Cracking was found in the weld between the end cap of the fuel element and the cladding after storage at room temperature \([16]\). Similar cracking was observed in welds in processing vessels used for making acetic acid or ethanol and in a chemical waste pipe \([7,17]\). In each case, cracking was not discovered until several months after welding. Cracks were initiated at small surface flaws such as a notch at the weld, porosity, a brittle oxygen-rich layer or a bolt thread. The cracking was found either at room temperature before the components went into service or after a series of thermal cycles during operation. The hydrogen concentration was within the specification, but that means that at room temperature hydrides could be present. Large residual crystal lattice strains, indicating large residual stresses, were measured by neutron diffraction \([17]\), Figure 7.

The maximum depth of a surface flaw, \(a_c\), that can be tolerated without crack growth by DHC, is estimated from Equation 4 \([18]\).

\[
a_c = \left(\frac{S}{1.21\pi}\right) \cdot \left(\frac{K_{IH}}{\sigma_D}\right)^2
\]

or a bolt thread. The cracking was found either at room temperature before the components went into service or after a series of thermal cycles during operation. The hydrogen concentration was within the specification, but that means that at room temperature hydrides could be present. Large residual crystal lattice strains, indicating large residual stresses, were measured by neutron diffraction \([17]\), Figure 7.

Two examples will be discussed to illustrate the principles.
the residual stresses by heat-treatment; a treatment of 530ºC (986ºF) for one hour soon after welding is sufficient to reduce these stresses by 60%, Figure 7, and increase the critical flaw depth to 1.3 mm (0.05”). This size of flaw should be found during inspection. The combination of stress-relieving within a certain time and careful inspection should eliminate crack initiation by DHC in these welds. This procedure has been incorporated into the Boiler and Pressure Vessel Code of the ASME[19].

STORING NUCLEAR FUEL WITHOUT DHC

Nuclear fuel for light water reactors (LWR) is clad in zirconium alloys such as ATI Zircaloys®, a Zr-1.5 Sn alloy. During its 4-6 years of service the cladding is subjected to hot pressurized water and neutron irradiation. Consequently the material is strengthened and corroded, leading to a large hydrogen pick up. On discharge from the reactor, the fuel is first stored in water, to allow the initial nuclear decay heat to be dispersed. To accommodate new spent fuel in the limited storage space, after a suitable time interval, it is desirable to store the fuel in dry facilities. The conditions during dry storage include:

• Very long residence times, with targets of 40-100 years.
• No irradiation damage from neutrons.
• An external fluid, usually an inert gas such as helium, with heat-transfer that is less efficient than the water used in reactor and in the storage pool.
• Heating from radioactive decay that declines with time; because of the relatively poor heat-transfer the cladding temperature is raised from ambient temperatures by several hundred degrees celsius, but because the heat-flux is about 1% or less of that during residence in the reactor, the temperature gradient through the cladding wall is very low, <1ºC/mm (<34ºF/mm).

The internal gas pressure from the original filler gas and fission products is greater than the ambient pressure — approximately atmospheric pressure — leading to tensile hoop stresses.

The temperature is highest at the start of storage being no higher than 400ºC (752ºF) — the maximum value recommended by the United States Nuclear Regulatory Commission (NRC)[20]; consequently the pressure and the hoop stresses are highest at the beginning.
Zircaloy fuel cladding is susceptible to DHC[22] and, if the correct conditions exist, can crack by DHC. Although the loading is mostly in plane stress, a stress gradient is setup at any flaw, which is sufficient to induce hydrogen migration to the flaw tip. About 275 ppm hydrogen are required to exceed TSSP at 400°C (752°F) and such high hydrogen concentrations have been observed in LWR cladding, for example, after a fuel burn-up of about 57 GWD/t, low-tin Zircaloy 4 contained between 600-820 ppm hydrogen[23]. Thus DHC would not be limited by lack of hydrogen during dry fuel storage.

Even with favourable stressing conditions, a maximum temperature, T₀, exists above which DHC cannot start, Figure 6. This temperature is around 290°C in unirradiated cladding material[23] but may be as high as 360°C (680°F) in irradiated material[11]. This phenomenon suggests that fuel that would start storage at the NRC-stipulated maximum temperature of 400°C (752°F) will be immune from DHC until the temperature reaches the critical temperature. This period of immunity is about three years, using the expected cooling curve[27], Figure 8. If T₀ depends on irradiation damage, its value may be reduced if the damage is annealed out during early storage. Thus the period of immunity may be much longer than estimated; if T₀ returns to 290°C (554°F), the period of immunity increases to about 12 years, Figure 8. The hoop stress will be simultaneously lowered, providing further protection. Once the period of absolute immunity is over, one then has to examine the stress conditions.

Calculation of the stress has to be based on the cladding thickness reduced by any hydride layer and the thickness of the oxide; the maximum corrosion allowance is 120 µm, corresponding to a metal loss of 80 µm (120/1.5 µm, where 1.5 is the Pilling-Bedworth ratio.) In typical cladding the initial outside diameter is 10 mm (0.39") and the wall thickness is 0.6 mm (0.024"); the thickness is reduced to 0.52 mm (0.021") by corrosion. One of the operating limits for fuel for a pressurized water reactor (PWR) is for the internal gas pressure, suggest that for cracks to propagate by DHC they would have to be through-wall and therefore detectable before storage started.

Experience of dry storage of nuclear fuel indicates no cracking for times ranging from 15-20 years[24,25], supporting the idea that DHC is unlikely during dry storage of LWR fuel after service.

The answers to the seven questions are summarized in Table 1 for these two examples. Despite the failures in welds and the spectre of cracking during fuel storage, zirconium alloys can be used free from DHC if the answers to most of the seven questions is “No”. Tensile stress must be carefully controlled if components contain hydrides or have the prospect of precipitating hydrides at a flaw.

### Table 1. Likelihood of DHC in welds and nuclear fuel dry storage.

<table>
<thead>
<tr>
<th>Questions</th>
<th>Welds in Zr-2.5Nb</th>
<th>Nuclear Fuel Dry Storage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Is the material susceptible to DHC?</td>
<td>Yes</td>
<td>Yes — except at beginning because of T₀</td>
</tr>
<tr>
<td>2 Is sufficient hydrogen present to form hydrides at a flaw?</td>
<td>Yes — at low temperatures.</td>
<td>Yes — from reactor operation</td>
</tr>
<tr>
<td>3 Was the temperature history conducive to DHC?</td>
<td>Yes — cooling after welding and plant operation.</td>
<td>Yes — except at beginning.</td>
</tr>
<tr>
<td>4 Were any temperature gradients present?</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>5 Are any sharp flaws present and if so, how large are they?</td>
<td>Yes — notch in weld, porosity, brittle oxygen-rich layer.</td>
<td>Yes — from operation.</td>
</tr>
<tr>
<td>6 Are large tensile stresses present?</td>
<td>Yes — residual stresses — can be removed by heat-treatment.</td>
<td>Yes — from internal gas.</td>
</tr>
<tr>
<td>7 Is the combination of 5) and 6) sufficient to exceed Kᵢₜ?</td>
<td>Yes — unless stress-relieved.</td>
<td>No — unless flaw through-wall.</td>
</tr>
</tbody>
</table>

Conclusion

The main features and basic mechanism of delayed hydride cracking in zirconium alloys have been outlined. Quantitative limits for cracking based on hydrogen concentration, temperature history, stress and flaw size are evaluated. Seven questions are posed to guide assessments for safe use of zirconium alloys without cracking.
References