

## HYDRIDE EMBRITTLEMENT IN ZIRCALOY COMPONENTS

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### ABSTRACT

Zirconium alloys are used in nuclear reactor cores under high-temperature water environment. During service, hydrogen is generated by corrosion processes, and it is readily absorbed by these materials. When hydrogen concentration exceeds the terminal solid solubility, the excess hydrogen precipitates as zirconium hydride ( $ZrH_2$ ) platelets or needles. Zirconium alloys components can fail by hydride cracking if they contain large flaws and are highly stressed. Zirconium alloys are susceptible to a mechanism for crack initiation and propagation termed delayed hydride cracking (DHC). The presence of brittle hydrides, with a  $K_{Ic}$  fracture toughness of only a few  $MPa\sqrt{m}$ , results in a severe loss in ductility and toughness when platelet normal is oriented parallel to the applied stress. In plate or tubing, hydrides tend to form perpendicular to the thickness direction due to the texture developed during fabrication. Hydrides in this orientation do not generally cause structural problems because applied stresses in the through-thickness direction are very low. However, the high mobility of hydrogen in a zirconium lattice enables redistribution of hydrides normal to the applied stress direction, which can result in localized embrittlement. When a platelet reaches a critical length it ruptures. If the tensile stress is sufficiently great, crack initiation starts at some of these hydrides. Crack propagation occurs by repeating the same process at the crack tip. Delayed hydride cracking can degrade the structural integrity of zirconium alloys during reactor service. The paper focuses on the fracture mechanics and fractographic aspects of hydrided material.

### 1. INTRODUCTION

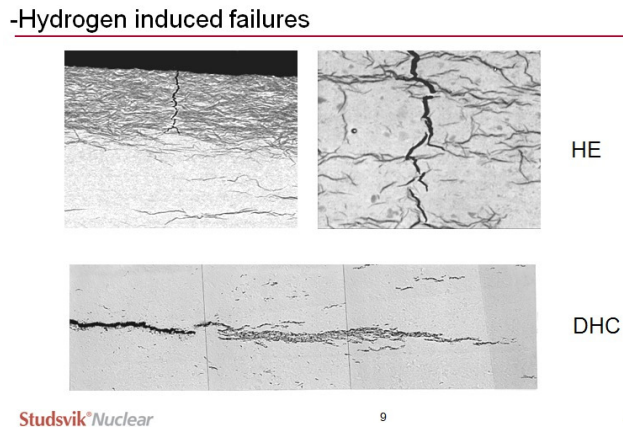
Zirconium alloys were selected as structural materials for water reactors because of their low thermal neutron capture cross-section, good resistance to corrosion in high temperature water and acceptable mechanical properties. These alloys are used for fuel cladding, pressure and calandria tubes, and fuel spacer grids. The performance of zirconium alloys in service has been generally satisfactory but some failures have been detected. The pressure to achieve higher burnups and higher reactor efficiencies is pushing the historically used alloys to the limits of their capabilities.

Zirconium alloys absorb hydrogen as a consequence of the corrosion reaction with water, as well as by other mechanisms that may be observed in defected fuel and where contact with dissimilar metals occurs. Hydrogen has very limited solubility in zirconium alloys, being less than 1 ppm at room temperature, about 80 ppm at 300 °C and about 200 ppm at 400 °C. Whenever the solubility limit is exceeded a zirconium hydride phase is precipitated, usually as platelets. This phase is brittle and it can have a deleterious effect on the mechanical properties of the alloy. The extent to which this embrittlement of the alloy occurs depends on the volume fraction of the hydride present, its orientation within the alloy (and with respect to

the principal tensile stress direction), and the degree of interconnectedness of the hydride platelets. Hydrogen redistributes easily at elevated temperatures, migrating down temperature and concentration gradients and up a tensile stress gradient

## 2. DELAYED HYDRIDE CRACKING

The concern about hydrogen uptake is related to the potential embrittlement of zirconium alloy component and thus to being able to predict when this might occur and evaluate its consequence. The worst embrittlement occurs at low temperature, especially when the normal of the hydride platelets are oriented parallel to the principal tensile stress, for example, a hoop stress in tubing. The next most serious situation arises when the solubility limit is exceeded in a component that is highly stressed for long periods of time. Examples of hydride-induced cracking are the delayed hydride cracks (DHC) (Figure 1) in pressure tubes. Fuel cladding, because it operates under heat flux, during normal operation can tolerate high average hydrogen concentrations, up to 1000 ppm, without significant embrittlement at operating temperatures, partly because the temperature gradient concentrates the hydride in the outer layers of the cladding leaving much of the wall thickness free of hydrides [1].



**Figure 1. Cracking aspects of hydrogen induced failures (Studsвик Nuclear).**

In some Zircaloy nuclear fuel cladding used in boiling-water reactors (BWR), hydride cracking is strongly implicated in long splits that allowed substantial leakage of fission products. Cladding in BWR's is usually a tube with diameter of about 10 mm, wall thickness of about 0.6 mm and length of about 4 m. The Zircaloy is usually recrystallized and in some designs of fuel rod the inside surface is lined with another zirconium alloy or pure zirconium, to prevent stress corrosion cracking by fission products, such as iodine. If the cladding wall is penetrated during operation, for example by fretting, water from the heat-transport system can enter into the fuel rod gap where steam is produced. Much hydrogen is generated because the steam oxidizes the fuel and the inside surface of the cladding, reducing the partial pressure of oxygen and leaving a gas rich in hydrogen. This process is called "oxygen starvation" [2].

With fuel expansion during power ramping, the hydrided cladding is stressed which leads to crack initiation. The cracks grow through-wall and may be over 1 m long. The lower bounds of the crack velocities were in the range  $4 \times 10^{-8}$  to  $5 \times 10^{-7}$  m.s<sup>-1</sup> based on assuming constant growth rates in the time between first detection of the defect and removal of the fuel. The mechanism of cracking appears to be a form of DHC perhaps exacerbated by a continuous additional supply of hydrogen from the steam inside the fuel element.

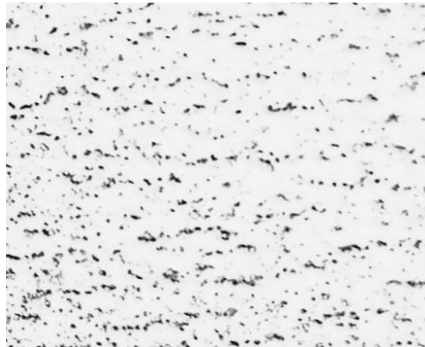
In a number of cases, rods of commercial BWR high burnup fuel, subjected to a power ramp in material test reactors, failed during a single step ramp test, with a crack starting from the outer surface of the cladding tube and propagating in the radial and axial directions. That was the case with segment rods installed in lead assemblies irradiated up to 5 cycles in Fukushima Danai BWR Nuclear Power Station N°. 2 Unit that were afterwards submitted to power ramp tests in a Japanese Material Test Reactor [3].

Spent fuel from Angra-I and Angra-2 nuclear plant is stored in pools close to the plants. Defective spent fuels were detected by visual inspection and confirmed by sipping tests. At least one hydride fuel failure was reported [4]

### 3. MATERIALS AND METHODS

To evaluate the DHC in fuel cladding materials the Pin-Loading Tension (PLT) technique developed at Studsvik Nuclear AB for thin-walled tubing will be used [5].

The zircaloy-4 specimens were cut from the tubing that was cold worked and stress relieved (480 C for 3.5 h + 410 C for 24 h); its mechanical properties at room temperature were: 0.2% yield stress (553 MPa), UTS (758 MPa) and total elongation (19%). The samples were previously charged with hydrogen (Fig.2), notched and pre-cracked in fatigue before testing (Fig. 3).



**Figure 2. Hydride microstructure of Zircaloy-4 cladding tube material.**

The PLT tests were done in a closed loop testing machine (Instron 1334) by load control and measuring the piston displacement (Load Line Displacement) using a data acquisition device to register the signals of load, displacement and temperature. An environmental chamber was used to get the temperatures required in the testing conditions with an accuracy of one degree Celsius. All the measurements of the fracture surface features were done using image analyzer software [6]. The DHC crack velocity corresponding to the Stage II in Figure 4 was measured. Crack growth was estimated on each crack from the average of nine equally spaced measurements; the value for the specimen,  $a_s$ , was the average of the values of the two cracks. Often an incubation period,  $t_i$ , was required before DHC started; cracking time,  $t_r$ , was taken as (time under load -  $t_i$ ). Crack velocity,  $V$ , in the axial direction of the cladding was  $a_s/t_r$ .

The value of Stress Intensity Factor,  $K_I$ , was calculated from Equation (1):

$$K_I = [P/(2t\sqrt{W})] f(a/W). \quad (1)$$

where

$P$  = load (N);

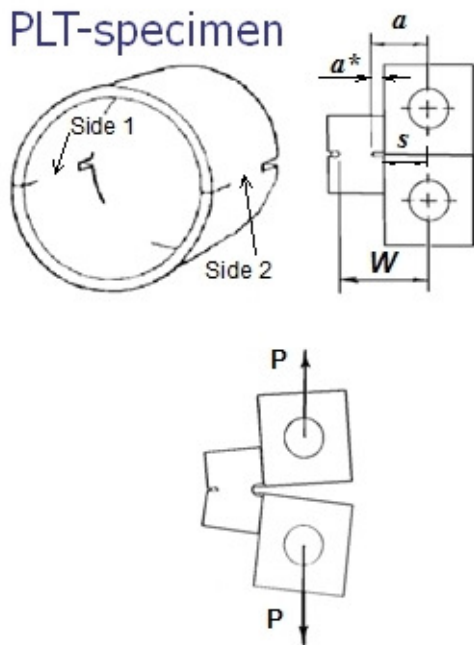
$t$  = wall thickness of the cladding (m);

$W$  = effective width of specimen (m),

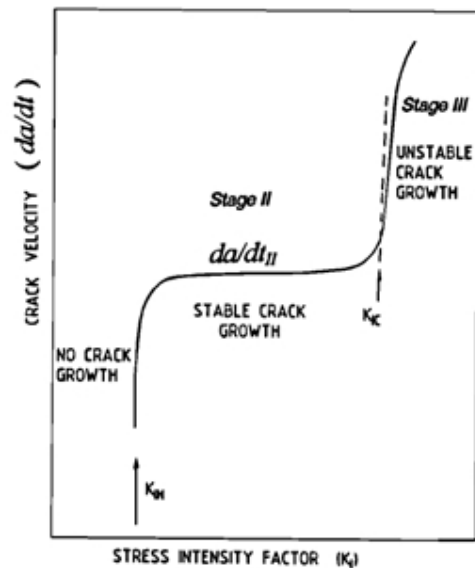
$a$  = effective crack length (m), being distance from load line to the crack tip;

$f(a/W)$  = geometry correction factor

$f(a/W) = 92.203 - 468.73(a/W) + 787.15(a/W)^2 - 360.99(a/W)^3$



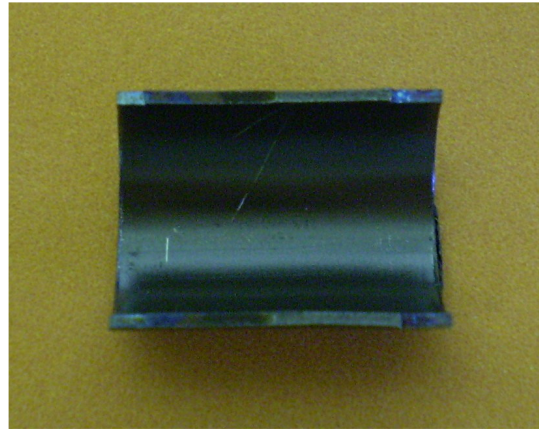
**Figure 3. PLT – specimen geometry and loading configuration.**



**Figure 4. Plot of the crack velocity as a function of the Stress Intensity Factor.**

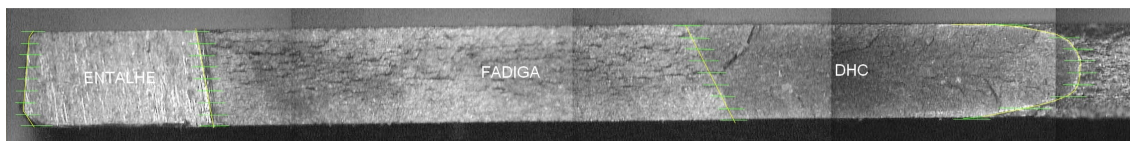
#### 4. RESULTS AND DISCUSSION

Figure 5 shows one half of a PLT Zircaloy-4 specimen broken in the testing at 300°C. There was no difficulty in cracking the specimens following the IAEA procedure [1], but the precise determination of the incubation time for DHC presented some problems. The samples were loaded for 20 to 40 hours and DHC cracks were about 2 mm. The DHC velocity obtained in 4 valid tests was in the range of 2.4 to 3.4 E<sup>-08</sup> m/s. Its average is 2.9 E<sup>-08</sup> m/s.



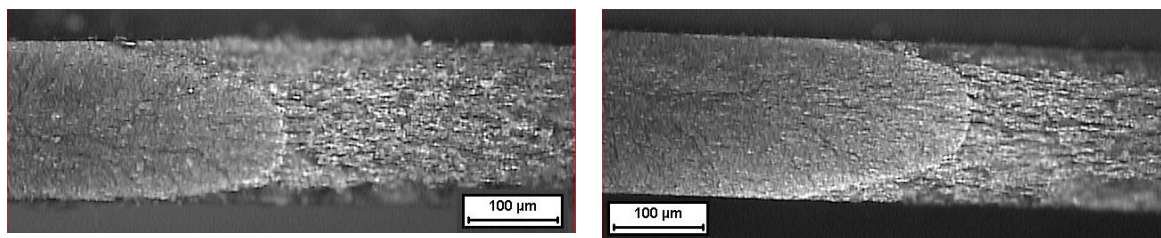
**Figure 5. PLT Zircaloy-4 specimen tested at 300°C.**

Figure 6 present a typical fractography of a PLT specimen subjected to DHC conditions. From left to right it is possible to distinguish 4 regions (bounded by green lines): notch region, pre-fatigued region, DHC region and mechanical overloading region.



**Figure 6. Typical optical fractography of PLT Zircaloy-4 specimen subjected to DHC conditions.**

In Figure 7 it is shown the fracture appearance of the DHC region (at left of each picture) for two different PLT specimens. The radial fracture marks follows a path from the center region (highest triaxial stress condition) to the borders region (pure plane-strain) via the hydrides particles.



**Figure 7. Details of the transition from DHC region (left) to the mechanical overloading region (right) in two PLT Zircaloy-4 specimens.**

## 5. CONCLUSIONS

Delayed Hydride Cracking (DHC) was shown to occur in Zircaloy-4 tubing specimens at temperatures close to 300°C and the average crack velocity was  $2.9 \text{ E}^{-08} \text{ m/s}$

## ACKNOWLEDGMENTS

Acknowledge the help of colleagues, Dr. Lalgudi V. Ramanathan and Olandir V. Correa

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