

DELAYED HYDRIDE CRACKING IN ZIRCALOY FUEL CLADDING – AN IAEA COORDINATED RESEARCH PROGRAMME

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The rate of delayed hydride cracking (DHC), V , has been measured in cold-worked and stress-relieved Zircaloy-4 fuel cladding using the Pin-Loading Tension technique. At 250 °C the mean value of V from 69 specimens was $3.3(\pm 0.8) \times 10^{-8}$ m/s while the temperature dependence up to 275 °C was described by $A \exp(-Q/RT)$, where Q is 48.3 kJ/mol. No cracking or cracking at very low rates was observed at higher temperatures. The fracture surface consisted of flat fracture with no striations. The results are compared with previous results on fuel cladding and pressure tubes.

KEYWORDS : Zircaloy-4, Delayed Hydride Cracking (DHC), Temperature Dependence

1. INTRODUCTION

A mechanism of flaw extension called Delayed Hydride Cracking (DHC) has been implicated in the failure of Zr-2.5Nb pressure tubes [1] and may contribute to long axial splits observed in some LWR fuel cladding [2,3]. The requirements for DHC are for sufficient time for enough hydrogen to accumulate to form, grow and crack hydrides at a stressed flaw tip. These requirements may be met in fuel cladding during reactor operation and during storage. Hydrogen is picked up during corrosion and only needs to exceed a concentration of 115 ppm to be present at 300 °C or 185 ppm to be present at 350 °C; fretting or interactions with the fuel may generate flaws; internal gas pressures or fuel expansion may impose tensile hoop stresses. The rate of DHC, V , is characterized by being almost independent of K_I once a threshold value, K_{IH} , is

exceeded and increases rapidly with increase in temperature; an upper temperature limit has been observed in Zr-2.5Nb pressure tube material above which DHC is very difficult.

The physical conditions for DHC in unirradiated Zircaloy fuel cladding are being studied in an inter-laboratory comparison organized by the IAEA. A similar exercise was successfully concluded on Zr-2.5Nb pressure tube materials [4]; by using a standard method of testing with compact toughness specimens, uniform sets of data were attained in laboratories in ten countries. The same principles are being applied for the testing of Zircaloy-4 fuel cladding in nine countries. Several methods are available for testing such thin-walled, small diameter material: a centre-cracked half-tube loaded in tension [5] a centre-cracked length of tube loaded by a wedge and mandrel (SPLIT test) [6] and the Pin-Loading Tension (PLT) technique [7]. The last method was chosen for this

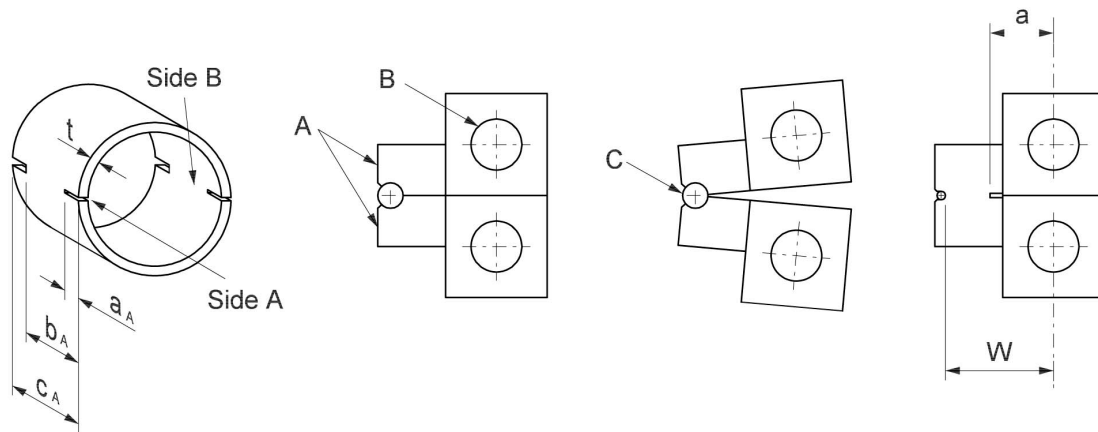


Fig. 1. Schematic Diagram of the PLT Specimen, Fixture, and Specimen-Fixture Assembly

programme because its loading was similar to that in a compact toughness specimen and was considered to be most amenable for technology transfer. The objectives of this programme were to evaluate the efficacy of the technology transfer and measure temperature dependence of the rate of DHC on a single material.

2. EXPERIMENTAL

The test programme had two phases. In the first phase, Studsvik prepared test fixtures and specimens from a batch of Zircaloy-4 cladding in the stress relief annealed (SRA) condition and each laboratory tested their allocation of specimens in a prescribed manner at a single temperature, 250 °C. Using this experience, during the second phase, each laboratory prepared their own specimens out of segments of similar tubing and tested them at two assigned temperatures.

The material used for the experiments was standard Zircaloy-4 that had been cold-worked 80% and stress-relieved at 480 °C for 3.5 h. The composition was Sn 1.26 wt.%, Fe 0.22 wt.%, Cr 0.10 wt.%, O 1220 ppm, Si 100 ppm and C 120 ppm. The tube dimensions were 9.52 mm outside diameter with wall thickness of 0.57 mm. The grains were elongated axially, with 5 to 10% recrystallized grains; the basal plane normals were concentrated about 30° from the radial direction with texture factors in the radial, transverse and axial directions of 0.66, 0.30, and 0.04, respectively. The strength of the material was measured with ring tensile tests as a function of temperature, T °C. Between 200 °C and 320 °C the UTS varied as $(683 - 0.71T)$ MPa. Depositing a layer of hydride on the surfaces electrolytically and diffusing the hydrogen in to the metal by annealing at 410 °C for 24 h added hydrogen for a total concentration of about 200 ppm. The specimen and test fixture are shown in Fig. 1. The 13 mm long

specimen (c_A) contained diametrically opposite axial notches at both edges with those at one end being sharpened by fatigue at room temperature for a starting length of a_A ; the notch at the other end provided an effective specimen length of b_A . The fatigue pre-cracking was done at 5-10 Hz with starting cycling loads of 200 N to 50 N. The maximum load was gradually reduced to 100 N as the crack progressed. The final load was chosen to be lower than the starting load for the DHC test, 160 N, so the plastic zone at the crack tip from fatigue did not interfere with DHC. About 20 000 cycles were required to produce a suitable starting crack.

The PLT-fixture consisted of two halves, which, when placed together, form a cylindrical holder, A. The diameter of the holder allowed it to be inserted into the specimen while maintaining a small gap. The fixture halves were loaded in tension through pins at B and rotated about a pin C at the ends of the cylindrical holder providing the similarity to the loading of a compact toughness specimen, but on two cracks. During a test, the specimen was heated to and held at a temperature 50 to 75 °C above the test temperature, cooled with no undercooling to the test temperature, then loaded to a K_I of about 15 MPa \sqrt{m} once the temperature was constant. The value of 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); see Fig. 1;

a = effective crack length (m); see Fig. 1.

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

Cracking was detected either by potential drop or by

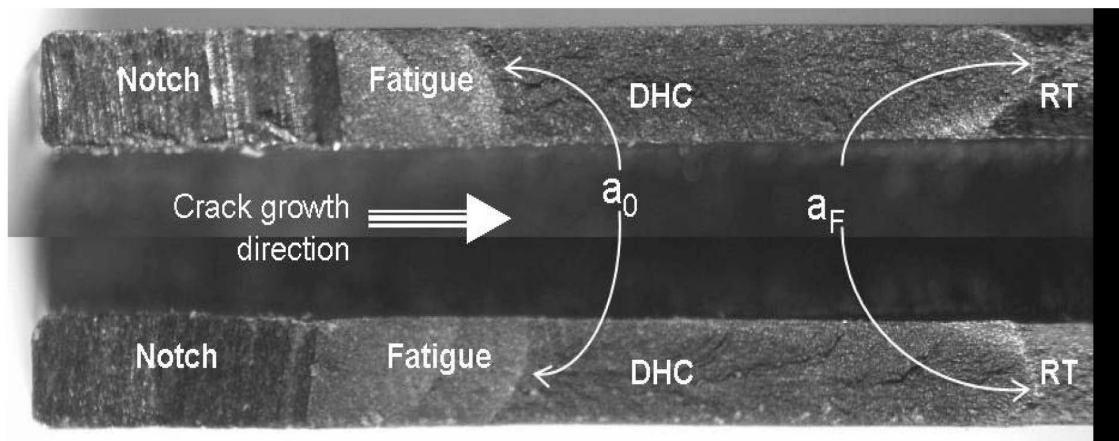


Fig. 2. View of the Fracture Surfaces of Unirradiated SRA Zircaloy-4 Specimen (205 ppm of Hydrogen). The Top and Bottom Edges are the Outside Surfaces of the Cladding. The Initial (a_0) and the Final (a_F) Length of the DHC Crack are Indicated as well as the Areas of Notch, Fatigue Pre-Cracking, DHC Crack Propagation and Room Temperature Fracture after the DHC Test (RT)

displacement (crack opening). Once the cracks had extended about 2 mm, the load was removed and the specimen cooled to room temperature and broken open. Often an incubation period, t_i , was required before DHC started; cracking time, t_r , was taken as (time under load - t_i). Crack growth by DHC, $a_F - a_0$ (Fig. 2), was estimated on each crack from the average of nine equi-spaced measurements or by measuring the area of fracture due to DHC and dividing by the tube wall thickness; the value for the specimen, a_s , was the average of the values of the two cracks. Crack velocity, V , in the axial direction of the cladding was a_s/t_r . A Scanning Electron Microscope (SEM) was used to examine the fracture surfaces of some specimens.

3. RESULTS

A typical fracture surface is depicted in Fig. 2 where the various stages of the test are visible as bands of different colour and roughness. Both fatigue cracks are characterized by a gently curved crack front, being longer on the inside surfaces because K_I is slightly larger than on the outside surface because of bending. The DHC fracture surface does not contain similar inside-outside characteristics because V is insensitive to K_I but has a region where the crack is held up at each specimen surface corresponding to a less constrained stress state.

The main fractographic feature is flat fracture associated with cleavage of hydride, Fig. 3. Striations, often associated with DHC in Zr-2.5Nb pressure tube material, were not observed.

The values of V at 250 °C in Zircaloy-4 obtained by each laboratory are summarized in Table 1. The range of the mean value of each set of data was from 2.03 to

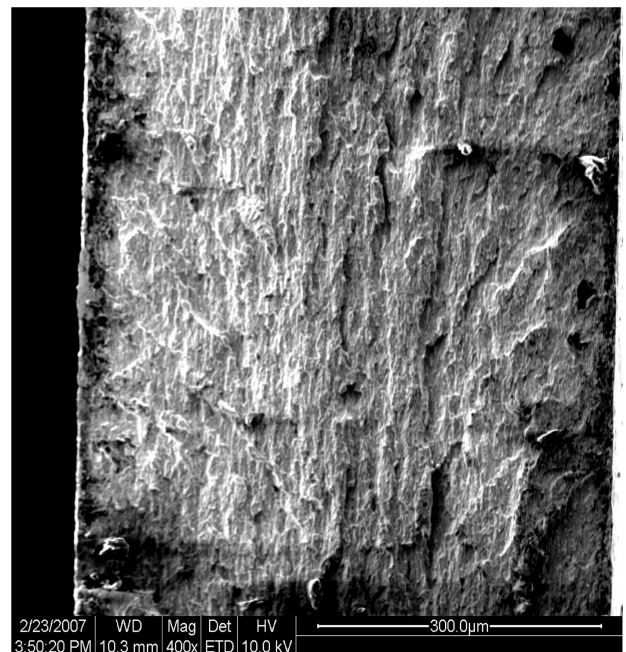


Fig. 3. Fracture Surface of Zircaloy-4 after DHC at 250 °C; Crack Growing from Bottom of Photograph. Note the Areas of Flat Fracture Corresponding to Broken Hydrides

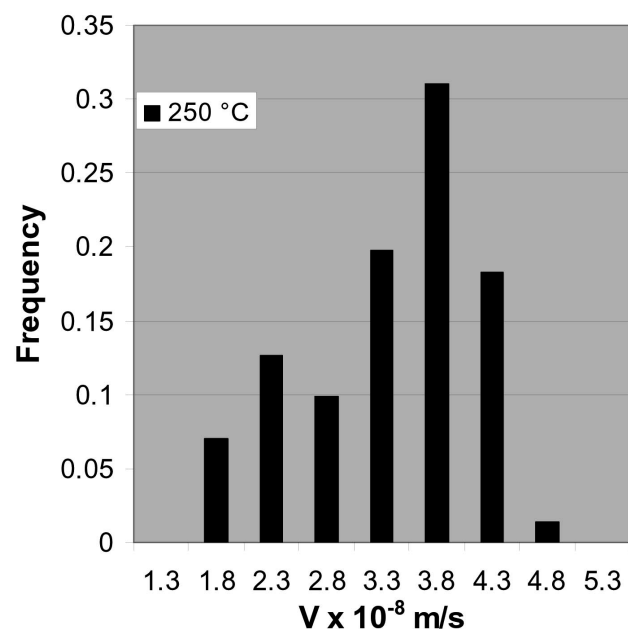
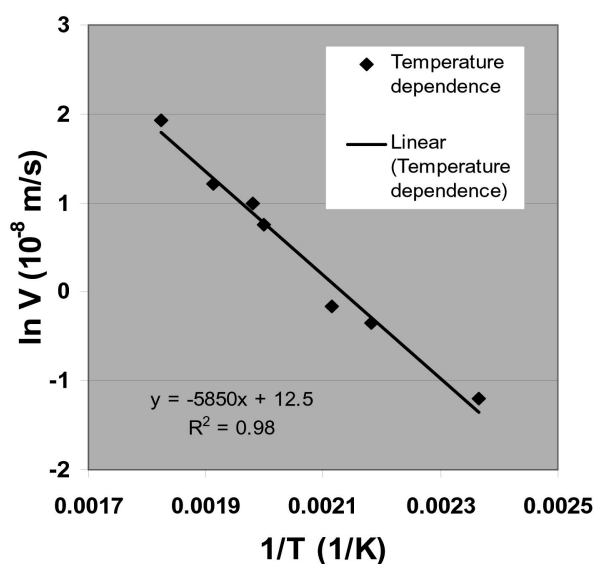
3.97×10^{-8} m/s while the standard deviation ranged from 0.27 to 0.76×10^{-8} m/s although most values were less than 0.5×10^{-8} m/s. The maximum and minimum values of V were 4.72×10^{-8} m/s and 1.57×10^{-8} m/s, respectively. The data from all 69 specimens had a mean value of 3.34×10^{-8} m/s and a standard deviation of 0.80×10^{-8} m/s. The distribution of the values of V is shown in Fig. 4.

Table 1. Summary of Values of Crack Velocity, V, at 250 °C for SRA Zircaloy-4 Fuel Cladding ($\times 10^{-8}$ m/s) from each Laboratory

Laboratory	A	B	C	D	E	F	G	H	I
Mean V	3.45	2.34	2.91	3.61	3.56	3.81	2.03	3.97	3.67
Standard deviation	0.48	0.39	0.45	0.76	0.36	0.7	0.27	0.34	0.32
Number of specimens	7	6	4	8	8	8	7	13	8

Table 2. Temperature Dependence of Crack Velocity, V, ($\times 10^{-8}$ m/s) for Delayed Hydride Cracking in SRA Zircaloy-4

Test temperature, °C	150	200	227	250	275	283	290	300
Crack velocity 10^{-8} m/s	0.3	0.86	2.1	3.3	6.8	4.7 or 0	0	0.55 or 0

**Fig. 4.** Distribution of Values of DHC Velocity, V, in SRA Zircaloy-4 Fuel Cladding**Fig. 5.** Temperature Dependence of DHC Velocity, V, in SRA Zircaloy-4 Fuel Cladding

$$V = A \exp(-Q/RT) \quad (2)$$

In contrast to the well-behaved values of V, the incubation times exhibited a very large variation. The mean value was 3520 s with a standard deviation of 4230 s, sometimes the cracking started immediately on loading whereas in some specimens 18000 s were required before the crack started to propagate. Some of this variation was attributable to the sensitivity of the crack detection system but most was probably caused by the variability in the stress state of the fatigue-sharpened crack.

The values of V at other temperatures are summarized in Table 2. Below 275 °C the values of crack velocity have a clear and highly correlated ($R^2 = 0.98$) temperature dependence described by Equation (2):

where Q = activation energy for cracking (kJ/mol),
T = test temperature (K),
R = gas constant (J/K.mol)
A = constant

and depicted in Fig. 5. Q has a value of 48.3 kJ/mol. At temperatures above 275 °C the rates declined with limited or no cracking observed at 283 °C and above, even when K_I was increased to about 18 MPa \sqrt{m} .

4. DISCUSSION

The results of these tests confirm that SRA Zircaloy

fuel cladding can crack by DHC. A consistent set of values was obtained in each laboratory indicating that the testing methodology had been accurately transferred.

The values of V compare favourably with those from pressure tubes made from Zircaloy [8, 9] and fuel cladding [5, 7], Fig. 6. The temperature dependencies characterized by Q were 69.5 kJ/mol and 55.5 kJ/mol for pressure tube materials [8, 9]. The discrepancies in both V and Q can be attributed to:

- differences in temperature and loading histories, which can contribute large variations in V ,
- small numbers of samples, which provides low confidence in the statistical evaluation of Q , and
- differences in microstructure, including texture, and strength.

The temperature dependence of DHC is dominated by the diffusivity, D , and solubility limit, C , of hydrogen in zirconium and to a lesser extent by the strength. To provide a guideline and to compare the behaviour of different materials in different conditions a useful normalization is that of Oh et al. [10]. Fig. 7 illustrates the normalization using UTS as the strength characterization (because that is the only strength quantity measured in ring tensile tests on fuel cladding in the current study). The values of D and C used for this exercise are derived from Sawatzky (Zircaloy [11] and Zr-2.5Nb [12]) and Kearns [13] while the values of UTS are mostly provided in the papers on DHC. The current results fit into the broad band of data on several different materials in different metallurgical

conditions, including irradiation [4, 7-9, 14] indicating that the DHC behaviour of fuel cladding is as expected from the experience with pressure tube materials.

The decline of DHC at high temperatures has been observed in both Zr-2.5Nb [15-17] and Zircaloy [14].

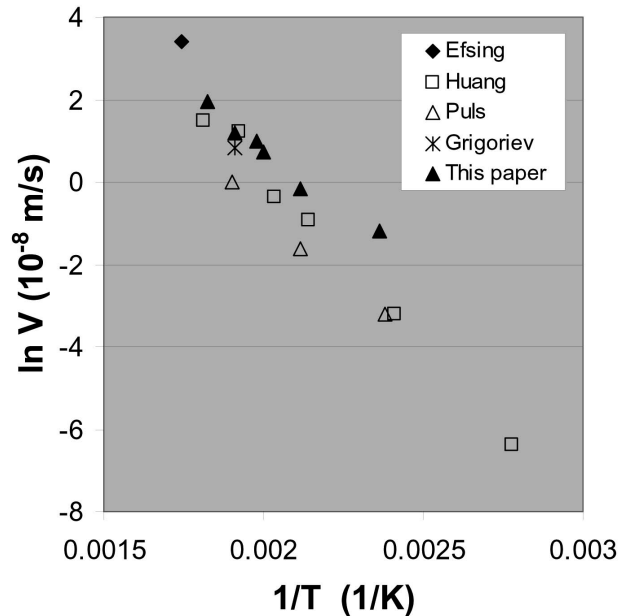


Fig. 6. The Temperature Dependence of V in Zircaloy

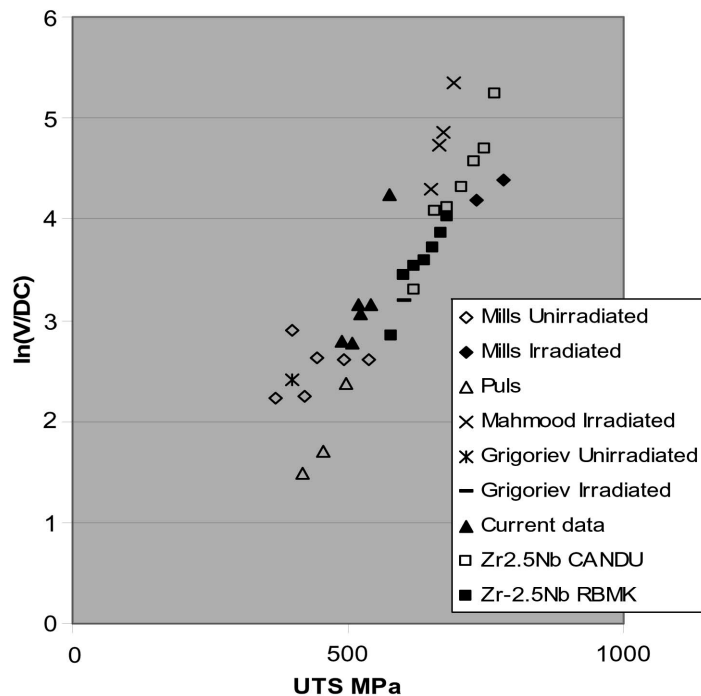


Fig. 7. Normalization of DHC Velocity, V , with the Diffusivity, D , and Solubility Limit for Dissolution, C

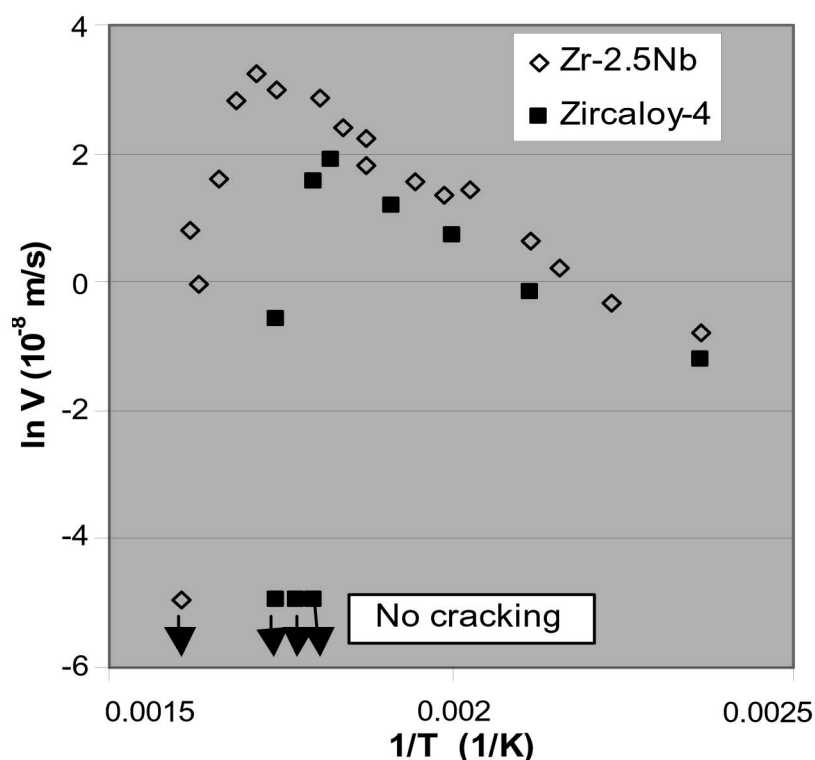


Fig. 8. High Temperature Crack Velocity Results for Cold-Worked Zr-2.5Nb [16] and SRA Zircaloy-4 [this Paper]

Fig. 8 is a direct comparison of the behaviour of cold-worked Zr-2.5Nb pressure tube material [16] and SRA Zircaloy-4 fuel cladding. In Zr-2.5Nb the crack velocity starts to deviate from the Arrhenius correlation at about 310 °C with no cracking detected at 350 °C while in the current Zircaloy-4 the initial deviation is at about 275 °C with little or no cracking at 300 °C.

The rate of DHC can be suppressed when:

- the hydrogen concentration is insufficient for hydrides to form at the crack tip. The current specimens contain 200 ppm hydrogen, which is sufficient for hydrides to be present at temperatures up to 360 °C, even on cooling to the test temperature. Thus the observed reduced rate of cracking is not caused by lack of hydride.
- the temperature history prevents hydrides from forming at the crack tip. Heating to the test temperatures may cause this situation, even if hydrides are present in the metal matrix [18]. In the current tests the test temperature was always attained by cooling from at least 50 °C above the test temperature, with no undercooling, so this effect is not the cause of the reduced velocity.
- K_{IH} becomes greater than the applied K_I . In Zr-2.5Nb, K_{IH} has little temperature dependence at temperatures below 300 °C but at higher temperatures it increases rapidly [17]. Zircaloy-4 likely behaves in a similar manner implying that K_{IH} increases to values greater than about

15 MPa√m above 280 °C. A corollary to this behaviour is that V and the crack suppression temperature will appear to depend on K_I . Close to the critical temperature, a small amount of evidence supports this conclusion. In Zr-2.5Nb the range of the suppression temperature increased from 280-313 °C to 328-359 °C when K_I was increased from 13 MPa√m to 17 MPa√m [15]. In the current study at 283 °C in one specimen no cracking was detected after 9000s at a K_I of 15 MPa√m but once K_I was increased by about 7% the crack progressed, but at a much reduced rate based on expectations from an extrapolation of Equation (2).

In this study, as in others on Zircaloy [5, 7, 8] the fractographic features called striations were absent. These observations are in marked contrast to the fractography of Zr-2.5Nb where striations are easily observed. Striations are bands across most of the width of a specimen, perpendicular to the crack growth direction, consisting of regions of ductile fracture bounding cleavage of hydride. They tend to remain a constant width and coplanar as the crack extends. In Zircaloy, the hydrides fracture on different planes along the crack front with ductile fracture between the brittle plates. The size of the brittle areas is variable so bands of consistent width are not formed. Microstructural features contributing to the difference in behaviour of the two materials are probably the finer scale

of the grains and presence of a β -phase in Zr-2.5Nb. The lack of striations with DHC in Zircaloy suggests that they are not a unique characteristic of DHC.

The maximum value of V in this study was 6.8×10^{-8} m/s at 275 °C, which is four to ten times lower than the rates estimated from splits in BWR's [3]. The current results are not suitable for direct application to the behaviour of fuel cladding because the material is unirradiated. The added strength generated by irradiation has two consequences: the crack velocity is increased by a factor between ten to fifty [7, 8, 19] easily agreeing with the rates observed in-reactor, and the high temperature decline in velocity is postponed to higher temperatures [17]. Other differences between cladding on an operating fuel element and these laboratory experiments include temperature gradients, which can affect crack velocity and response to temperature history [20]. Nevertheless, these data provide a basis from which to build a data set for future reference.

5. CONCLUSIONS

The PLT technique for measuring DHC has been transferred to eight IAEA member states. Tests on CWSR Zircaloy-4 fuel cladding have provided reliable values of crack velocity that had an Arrhenius-type temperature dependence up to 275 °C followed by a drop off in rate at higher temperatures. No striations were observed suggesting that they are not a fundamental feature of DHC. The current results were compatible with those obtained in the first part of this programme on Zr-2.5Nb pressure tube material, once the differences in microstructure and strength were taken into consideration. This agreement provides confidence in the PLT method for estimating DHC properties in fuel cladding.

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