

## **Delayed Hydride Cracking Velocity of CANDU Zr-2.5Nb Tubes in High Temperature Water**

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This study focuses on an understanding of the environmental effect on delayed hydride cracking velocity (DHCV) of CANDU Zr-2.5Nb tubes. To simulate DHC susceptibility of the Zr-2.5Nb tubes in reactor operating conditions, DHC tests were successfully carried out in pressurized water at 180 and 250 °C using a self-designed autoclave for the first time. Using 17 mm compact tension specimens electrolytically charged to 34 and 60 ppm H, 3 to 7 DHCV data were determined in water at both temperatures and compared to those determined in air that were already confirmed to be valid through a round robin test on DHCV of Zr-2.5Nb tubes sponsored by a IAEA coordinated research program. The pressurized water environment has little effect on DHCV of Zr-2.5Nb tube in water at both temperatures even though DHCV is slightly lower in water than that in air. The lower DHCV of the Zr-2.5Nb tube during short-term tests is discussed in viewpoint of the cooling rate from the peak temperature to the test temperature.

**Key Words** : Zr-2.5Nb, pressure tubes, DHCV, environmental effect, autoclave, hydrogen concentration

### **1. Introduction**

Currently, Zr-2.5Nb alloys are being used as pressure tube material in heavy water reactors due to excellent features such as high strength and ductility at high temperatures, superior corrosion resistance and, most of all, a lower neutron cross absorption section. However, the Zr-2.5Nb pressure tubes pick up part of the hydrogen produced by their corrosion in high temperature

water and become susceptible to delayed hydride cracking (DHC) when enough hydrogen is accumulated in them. Especially, when a Zr-2.5Nb tube has rolled joints with large tensile residual stress due to an improper joining process or sharp surface flaws, a crack grows to the through-wall crack by DHC, causing leaking of heavy water out of the tube [1]. Actually, there have been many reported failures in pressure tubes due to DHC in Canada since the 1970s

[2,3,4]. Even in Korea, three Zr-2.5Nb pressure tubes were replaced due to DHC concern from the Wolsong Unit 1 nuclear power plant in 1994 [5].

Much attention has been paid to evaluating DHC velocity (DHCV) and the threshold stress intensity factor,  $K_{IH}$  of Zr-2.5Nb tubes operating in reactors. It is because  $K_{IH}$  determines the allowable size of surface flaws and DHCV determines the time to unstable fracture after the formation of a through-wall crack, thus determining a safety margin in association with the leak-before-break criterion. The problem with DHCV of the Zr-2.5Nb pressure tubes is that DHCV data reported up to date has a big scatter, depending on the test conditions [6-9]. In other words, a standard procedure to determine DHCV of Zr-2.5Nb tubes is yet to be established. It is because the DHC phenomenon has not been clearly understood. Recently, a round robin test has been conducted under an IAEA coordinated research program to establish a standard test method for DHCV of Zr-2.5Nb pressure tubes. Through the round robin test, a large number of qualified data of DHCV of Zr-2.5Nb tubes were successfully obtained with a 95% confidence level [10], which will be recognized as a set of standard data for DHCV of the CANDU Zr-2.5Nb tube.

Up to now, most DHCV data for Zr-2.5Nb tubes have been determined in air, though the pressure tubes are exposed to high temperature water during their operation in reactors. To simulate DHC of Zr-2.5Nb tubes in reactor operating conditions, thus, it is required to run the DHC tests in high temperature water with a view to evaluating the environmental effect on DHCV of the Zr-2.5Nb tubes. Hence, the objective of this study is to conduct DHC tests in high temperature water for the first time to verify the effect of the environment on DHCV of the Zr-2.5Nb tube, or if there is a difference in DHCV either in air or in high temperature water.

## 2. Experimental Procedures

### 2.1. DHC Tests

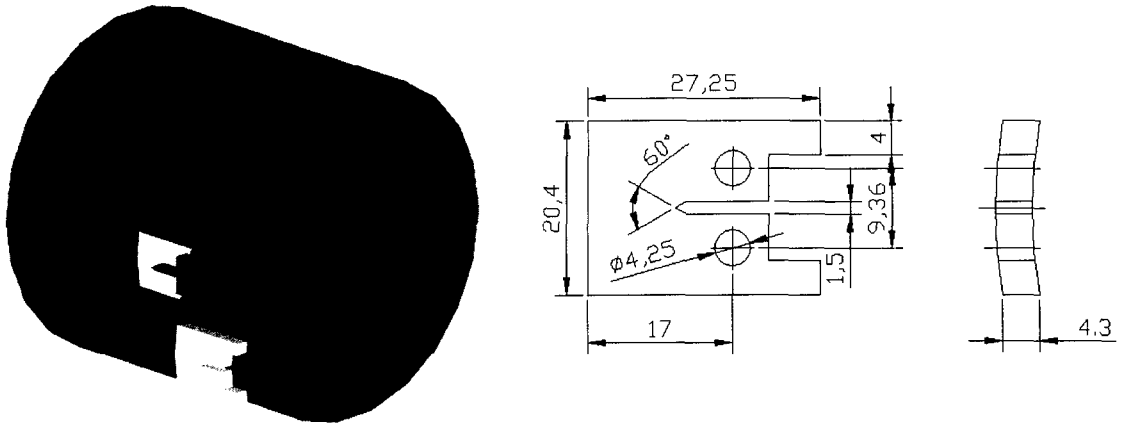
A tube ring was cut out of a CANDU Zr-2.5Nb tube whose composition was as described in Table 1. They were subjected to electrolytic charging of hydrogen to form a thick hydride layer on their surfaces followed by annealing in a salt bath where the specimen temperature could be controlled to  $\pm 0.5$  °C. The hydrogen concentration of the CT specimens was controlled at 34 ppm or 60 ppm, depending on the DHC test temperature, 182 or

**Table 1. Chemical Composition of the Used Zr-2.5Nb Pressure Tube**

Element	Nb	O	Fe	Sn	C	Zr
Content	2.7 wt.%	1020 ppm	0.086 wt.%	24 ppm	89 ppm	balance

**Table 2. Cooling Rate During the DHC Tests in Water and Air**

Test Temperature (°C)	Environmental Conditions	Cooling Rate (°C/min.)
250	Water	1.45
	Air	0.36
182	Water	0.98
	Air	0.79

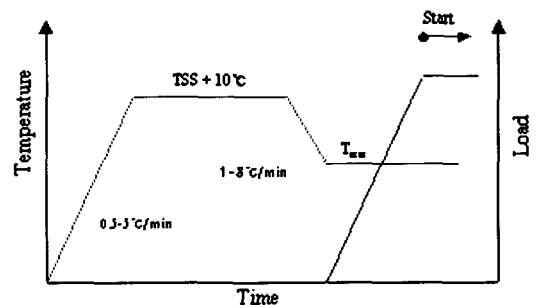


**Fig. 1. (a) Configuration and (b) Dimensions of the CT Specimens Taken from a CANDU Zr-2.5Nb Tube**

250 °C, respectively. The details of the hydrogen charging procedure are reported elsewhere [11]. 17 mm compact tension specimens were cut out of the hydrided tube ring as shown in Fig. 1. A pre-fatigue crack of 1.7 mm was introduced in the CT specimens using an Instron 8501 to have the ratio of the fatigue length and the CT length ( $=a_0/W$ ) equal to 0.5. The applied stress intensity factor was  $12 \text{ MPa}\sqrt{\text{m}}$  at the initial stage of the pre-fatigue crack and decreased to  $10 \text{ MPa}\sqrt{\text{m}}$  after the fatigue crack grew to 1.7 mm.

DHC tests were carried out in a self-designed autoclave containing water at 182 and 250 °C with an aim to simulate pressurized water at high temperatures in CANDU reactors. The applied pressure in the autoclave was 1.4 MPa at 182 °C and 4.8 MPa at 250 °C. Fig. 2 shows the thermal and loading cycles applied during DHC tests in the autoclave that were the same as those during DHC tests in air [12]. The CT specimens were heated up to the peak temperature by 0.5-1 °C/min, held there for 1 h and cooled down to the test temperature followed by applying the load 30 minutes after reaching the test temperature. The peak temperature was set at 10 °C higher than the temperature of terminal solid solubility for

dissolution (TSSD) of hydrogen as shown in Table 2. It should be noted that the cooling rate from the peak temperatures to the test temperatures were controlled at 0.98 to 1.45 °C/min in water that is slightly faster than that applied in air or 0.36 to 0.79 °C/min as shown in Table 2. The stress intensity factor of  $15 \text{ MPa}\sqrt{\text{m}}$  was applied at the beginning of DHC tests either in air or in high temperature water for DHC tests to be carried out in the second stage where DHCV becomes constant independent of applied stress intensity factor. The applied load corresponding to  $15 \text{ MPa}\sqrt{\text{m}}$  was determined in compliance with [11]. Constant 6 amperes were applied to



**Fig. 2. Thermal and Loading Histories Which CT Specimens Experienced during DHC Tests**

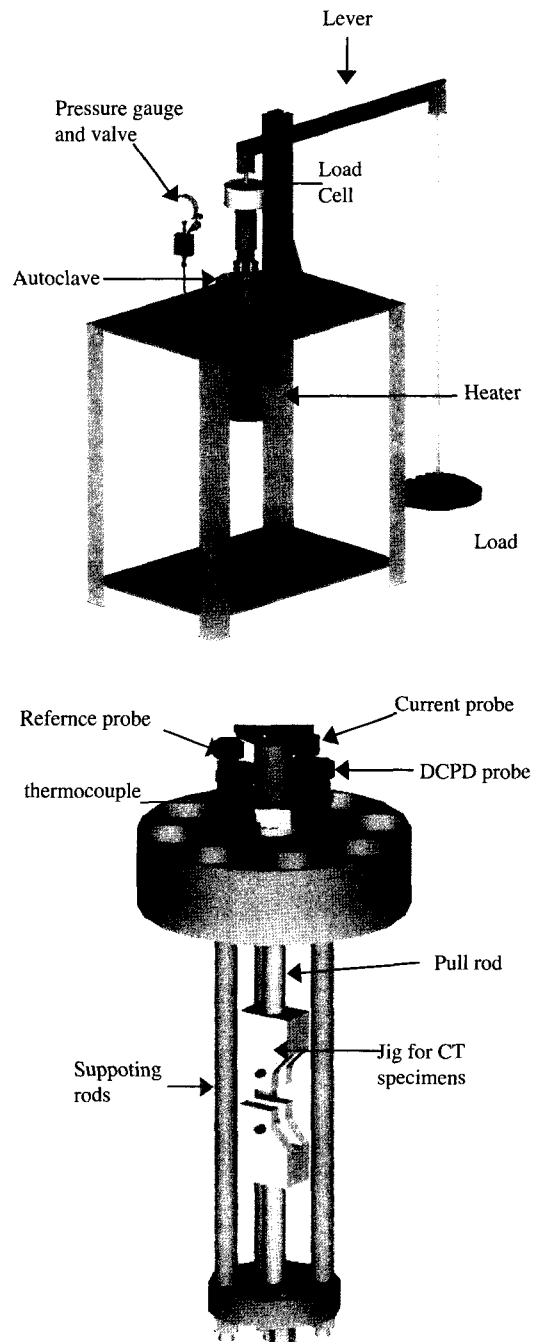
the CT specimens and the voltages were measured directly on a recorder and a multi-meter. Using a relation between the direct current potential drop (DCPD) and the crack length, DHC tests were terminated after the crack length grows to 1.5 to 2 mm. Then, after the CT specimens were broken up, the fatigue crack length and the DHC crack length were determined using the 9-point measurement directly on a microscope (micro-Vickers hardness, Model No. HMV-2000). The measured lengths of the fatigue crack and the DHC crack were used to accurately determine the initial  $K_I$  and the final  $K_I$  at the end of the testing. DHCV was determined from the measured length of the DHC crack divided by a time difference between the crack initiation time and the time at the termination of the DHC tests:

$$DHCV = \frac{\text{crack length}}{\text{time}_{\text{termination}} - \text{time}_{\text{initiation}}}$$

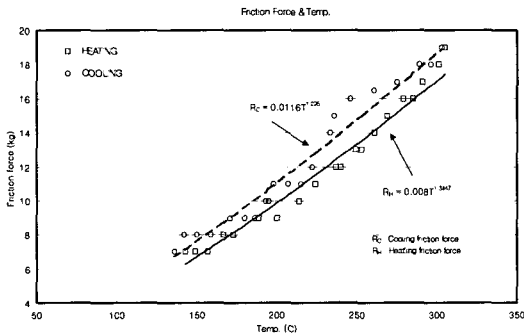
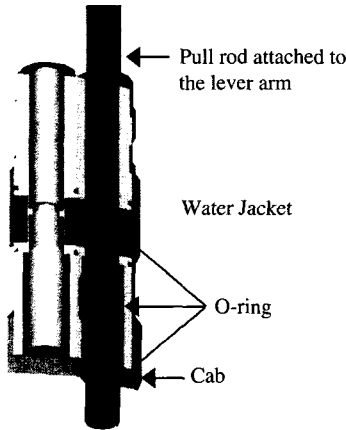
where the  $\text{time}_{\text{termination}}$  and the  $\text{time}_{\text{initiation}}$  represent the time when the DHC tests were terminated and the time to begin the growth of DHC crack, respectively.

## 2.2. DHC Test Equipment Simulating High Temperature Water Conditions

Specially designed DHC test equipment was developed where DHC tests can be conducted in pressurized water of high temperature as shown in Fig. 3. Tensile load was applied to the CT specimens using a lever arm with the load ratio of 5: 1, which was automatically recorded using a load cell attached. The CT specimens were put inside an autoclave filled with 400 ml of water along with the pull rod that was fed through a lid as shown in Fig. 3b. To prevent any leak from the moving pull rod during the DHC tests, three O-rings were installed on the pull rod and cooled by the installed water jacket as shown in Fig. 4.



**Fig. 3. Self-designed DHC Tester: (a) Assembled Autoclave Loaded by a Lever Arm and (b) the Details of the Lid Supporting the Jigs, a Pull Rod and the CT Specimens**



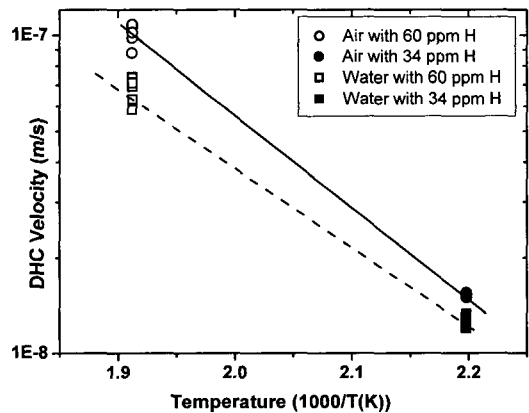
**Fig. 4. (a) Sealing of the Pull Rod by O-rings and Friction Forces on the Pull Rod with Temperatures**

Since these O-rings applied some friction forces on the pull rod, the friction force by the O-rings was determined as a function of temperature as shown in Fig. 4b [13]. Then, the applied load was corrected to compensate a loss of the applied load by the friction force. The temperature of the CT specimen exposed in the water was recorded through a thermocouple welded to the crack tip of the CT specimen, which was monitored by a computer. A metal gasket was installed between the lid and the autoclave to prevent any leak. This self-designed DHC test equipment was qualified to maintain leak-tightness well after running for 10 days at 320 °C under 13.8 MPa.

### 3. Results and Discussion

DHCV of the CANDU Zr-2.5Nb tube was determined in water at 182 and 250 °C and compared with that measured in air as shown in Fig. 5. Here, the DHCV data in air were taken from our own data conducted for the IAEA round robin tests on DHCV of Zr-2.5Nb tubes [12]. To reliably evaluate the environmental effect on DHCV, 3 to 7 DHC data were obtained in air and in water as well. Over the temperature range from 182 to 250 °C, DHCV of the Zr-2.5Nb tube was found to be slightly lower in water than that in air. However, this difference is rather small enough to be bounded within ±95% confidence level of the DHCV data as shown in Fig. 6 that have been determined from the set of 166 data produced for the IAEA round robin test in air on DHCV of a CANDU Zr-2.5Nb tube [10]. Therefore, we conclude that the water environment has little effect on DHCV of Zr-2.5Nb.

It is worth noting that all the DHC test conditions either in air or pressurized water are the same but small difference in the cooling rate from the peak temperature to the test temperature. Therefore, the consistently lower



**Fig. 5. DHCV of the CANDU Zr-2.5Nb Tube in Air and Water at 182 and 250 °C**

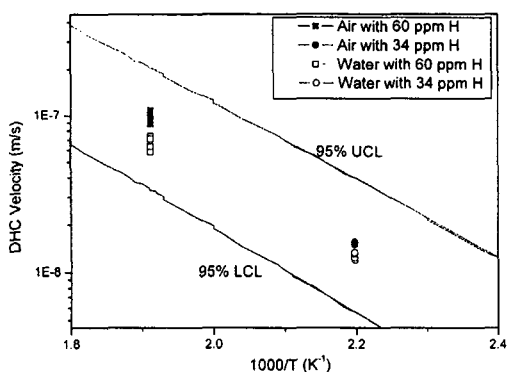


Fig. 6. Comparison of DHC Velocity of CANDU Zr-2.5Nb Tube in Water and Air with the Upper and Lower 95% Confidence Limits

DHCV in water than in air may likely be attributed to a higher cooling rate in water from the peak temperature to the test temperature as shown in Table 2. Further, a difference in the cooling rate between water and air became larger especially at 250 °C. Since a higher cooling rate increases the temperature of terminal solid solubility for precipitation (TSSP) of hydrogen [14] or facilitates the precipitation of hydrides in other words, this will decrease the hydrogen concentration in solution as shown in Fig. 6. During cooling-down to the test temperature from the peak temperature, the hydrogen solvus line follows the A-B<sub>r</sub>-C<sub>r</sub> route for the slow cooling rate and the A-B<sub>f</sub>-C<sub>f</sub> route for the fast cooling rate, respectively. At the test temperature, the bulk region and the crack tip will have the supersaturated hydrogen concentration: either C<sub>s</sub> or C<sub>t</sub> depending on the cooling rate. As soon as tensile stress is applied, however, hydrides start nucleation only at the crack tip, reducing the supersaturated hydrogen concentration at the crack tip to TSSD (represented as D). Thus, there develops a gradient of the hydrogen concentration between the crack tip and the bulk region as suggested for the first time by Kim et al [15]. Hence, the concentration gradient at the test temperature

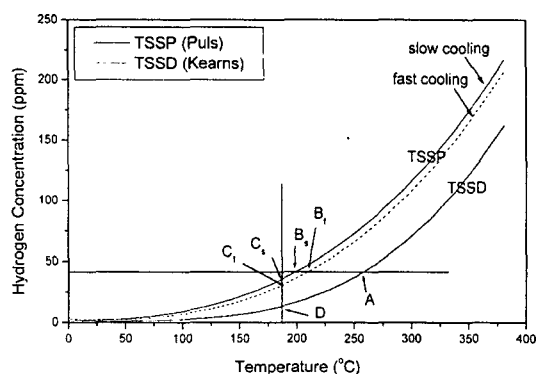


Fig. 7. Effect of the Cooling Rate on the Terminal Solid Solubility of Hydrogen for Precipitation and its Effect on a Gradient of Hydrogen Concentration in Solution Between the Crack Tip and the Bulk Region

between the bulk region and the crack tip becomes slightly less at the higher cooling rate: C<sub>s</sub>-D > C<sub>r</sub>-D as shown in Fig. 6. In other words, the driving force for DHC becomes less with the higher cooling rate. This will result in lower DHCV at the fast cooling rate. However, a small difference in the driving force will lead to the small difference in DHCV as shown in Fig. 5. It should be noted that a larger difference in the cooling rate at 250 °C between water and air yields a larger difference in DHCV compared with a smaller difference in DHCV at 182 °C with a small difference in the cooling rate. However, the quantitative evaluation of how sensitive DHCV will be to the cooling rate is yet to be made.

In case of the current experiment where a Zr-2.5Nb tube was exposed in water at lower temperatures for a very short time, the Zr-2.5Nb tube had little corrosion so that the crack will have little chance of being exposed to the evolved hydrogen. However, if corrosion of the Zr-2.5Nb tube is accompanied during long-term DHC tests as in the reactors, then, some hydrogen evolved during corrosion will move toward the crack tip, probably leading to some acceleration of DHCV.

This inference comes from the fact that hydrogen atmosphere enhances DHCV by 4 to 5 orders of magnitude [16]. Thus, the DHC tests to simulate the effect of evolved hydrogen accompanied by corrosion need to be conducted in pressurized water containing dissolved hydrogen.

#### 4. Conclusions

To simulate DHC of Zr-2.5Nb tubes in reactors, for the first time, DHC tests were successfully conducted on a CANDU Zr-2.5Nb tube in pressurized water at 182 and 250 °C using a self-designed autoclave which was qualified to maintain leak tightness at 320 °C under 13.8 MPa for 10 days. The pressurized water environment has little effect on DHCV of Zr-2.5Nb tube though slightly lower DHCV was observed in water compared to that in air. Thus, from the standpoint of the LBB safety criterion, DHCV of the Zr-2.5Nb tube in air seems to be more conservative. The higher cooling rate from the peak temperature to the test temperature in water, is likely to cause a slight decrease in DHCV of the Zr-2.5Nb tube in water compared to that in air. It is because the faster cooling rate increases the TSSP temperature, lowering the hydrogen concentration in solution at the bulk region and the concentration gradient of hydrogen between the crack tip and the bulk region. However, since the hydrogen evolution and pick-up processes are accompanied during DHC of Zr-2.5Nb tubes in reactors, other long-term DHC tests are required to verify the effect of evolved hydrogen on their DHC resistance.

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