

# Precipitation Temperatures and DHC Velocities

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## Summary

Delayed Hydride Cracking (DHC) of zirconium alloys has led to several failures of components in nuclear reactors and chemical plants. The process requires hydrides to form, and hence any understanding requires knowledge of hydride precipitation temperatures. Generally, these temperatures are determined using experimental techniques that do not involve cracking; hence, there is some ambiguity in relating these temperatures to cracking. With the advent of more precise cracking experiments, it is now possible to determine precipitation temperatures directly from cracking velocity measurements. In this study, precipitation temperatures were determined from crack velocity measurements, and compared with values determined from Differential Scanning Calorimetry (DSC), which form the basis of current standards. It was found that DSC onset temperatures provide the best indication of the precipitation temperature. In addition, the Diffusion First Model for DHC velocity is shown to provide better predictions, over a wide range of concentrations and temperatures, when the temperature in the standard TSSP equation is shifted to the onset temperature.

## 1. Introduction

Hydrogen ingress can occur in zirconium alloys during service in nuclear reactors as part of the corrosion process, or through contact with other metals that convey hydrogen from afar. Hydrides are formed when the alloy is cooled below the precipitation limit, or when the concentration of hydrogen in solution reaches the precipitation limit, which is called the Terminal Solid Solubility for Precipitation (TSSP) of hydrogen. Hydrides are brittle and can crack under certain conditions. If the cracking is time dependent it is called Delayed Hydride Cracking (DHC) and is the mechanism of fracture responsible for several failures of zirconium alloy components in nuclear reactors and chemical plants. This cracking is time-dependent because it requires movement of hydrogen in solution to form hydrides. There are three basic steps involved in DHC. These are (1) the diffusion of sufficient hydrogen to nucleate a hydride at the stress raiser followed by (2) growth of the hydride until (3) fracture occurs, if the applied stress is above some limiting value. These steps then repeat as the crack grows. This process has been very difficult to model well [1]. The velocity of the propagating crack, once it starts to grow, can be modeled with the assumption that it is limited by the diffusion of hydrogen to the crack tip. Hydrogen diffuses because of a gradient in the chemical potential, which can be written in terms of gradients of concentration, temperature, and stress. The Diffusion First Model (DFM) is a version of this interpretation that has successfully predicted many different independent experimental observations [1]. The DFM uses an equation for the TSSP concentration in terms of precipitation temperature; historically, equations for TSSP have not been well characterized in the literature. The current equations for TSSP are determined with

Differential Scanning Calorimetry (DSC) and the assumption that the precipitation temperature is equal to the temperature at which the heat-flow curve changes the most with temperature, which is known as the maximum slope temperature [2]. The current TSSP equations based on the maximum slope temperature provide good predictions of DHC when used in the DFM [1]. However, the DFM is very sensitive to TSSP: the peak velocity is predicted to occur at the TSSP temperature, and predictions are determined from small differences between two large numbers, one of which is the TSSP concentration. Thus, the sensitivity of DHC velocity to the choice of TSSP temperature suggests that experimental velocities could be used to determine TSSP temperatures. In this study, crack velocities will be used to determine the TSSP temperature. The result will be compared with DSC cooling measurements and metallographic images of hydrides in the fracture surfaces.

## 2. Experimental

The material used in this study was taken from a Zirconium-2.5% Niobium CANDU™ pressure tube. Hydrogen was added by electrolysis and annealing to a concentration of 72 ppm. Compact tension specimens were machined with notches cut into the specimens that were pre-fatigued to create a sharp crack. All of the notches were parallel to the longitudinal tube direction, as were the cracks. During testing, the specimens were brought to a maximum temperature of 360 °C for an hour, to dissolve all the hydrogen, and then cooled to their respective test temperatures at a rate of 1 °C per minute. Specimens were then held at the test temperature for an hour before the load was applied. The applied load was held constant during each test with an initial stress intensity factor of  $17 \text{ MPa}\sqrt{m}$ . At the end of the test, specimens were unloaded then air-cooled to room temperature and broken open so that the fracture surfaces could be examined by metallography. The rate of crack growth was estimated from the area cracked, divided by the specimen thickness, 6.3 mm, and divided by the cracking time. Details of the DHC experiment have been published previously [3].

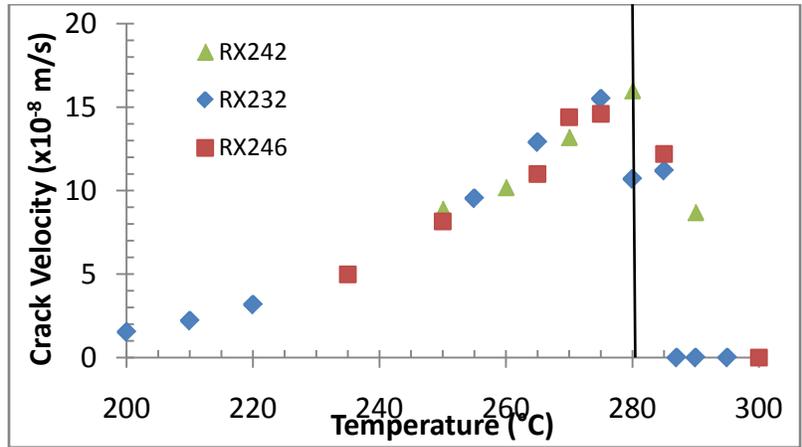
Differential Scanning Calorimetry was done with a TA Instruments Model Q20 V24.9. Samples cut from the compact-tension specimens were heated to 400 °C and then cooled at 10 °C per minute and the differential heat flow recorded.

## 3. Results and Discussion

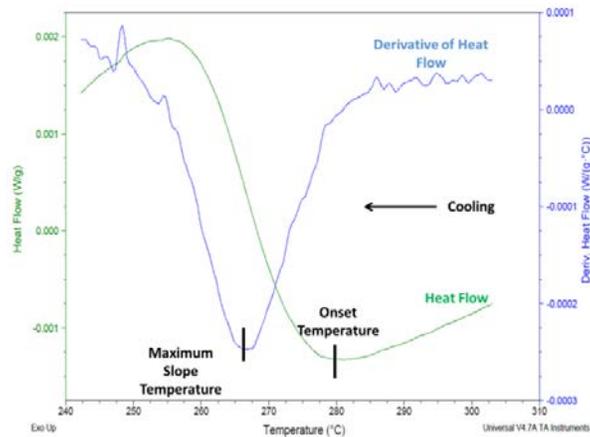
Measured DHC velocities are shown in Figure 1 for different test temperatures, each of which were preceded by heating to 360 °C to dissolve all of the hydrides. The different symbols refer to specimens made from different sections of the pressure tube. The vertical line in the figure shows the onset temperature defined in the DSC heat-flow curve shown in Figure 2 for material containing 72 ppm hydrogen. The onset temperature is the temperature where the heat flow curve first begins to move as hydrides precipitate on cooling. In Figure 2, the maximum slope temperature, which is the standard value used to define precipitation [2], is at a lower temperature than the onset temperature. The DSC onset temperature is closer than the maximum slope temperature to the temperature of the maximum DHC velocity.

Figure 3 shows crack fracture surfaces for specimens tested above and below the onset temperature. In general, the fracture surfaces contained bulk hydrides if the test temperature was below the onset temperature, but did not contain bulk hydrides if tested above. It is not necessary to have hydrides in the bulk for DHC to occur, however, hydrides will be present in

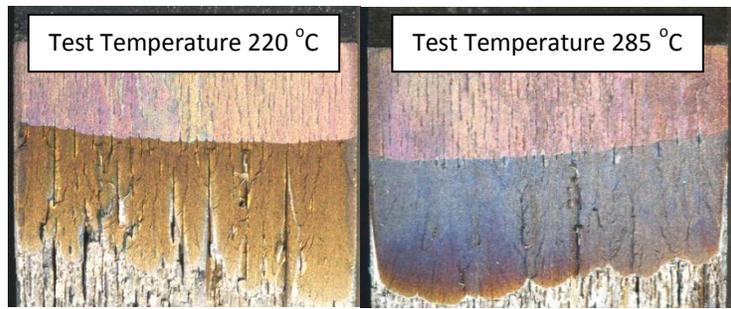
the bulk if the test temperature is below the precipitation temperature, and absent if above. Thus, the observation of hydrides for temperatures below the onset, but not above, shows the onset to be the precipitation temperature for bulk hydrides during DHC.



**Figure 1: DHC Crack Velocities as a function of temperature. Vertical line is the DSC onset temperature from Figure 2.**



**Figure 2: DSC Curve on cooling a tested Zr-2.5Nb sample (RX246) containing 72 ppm**

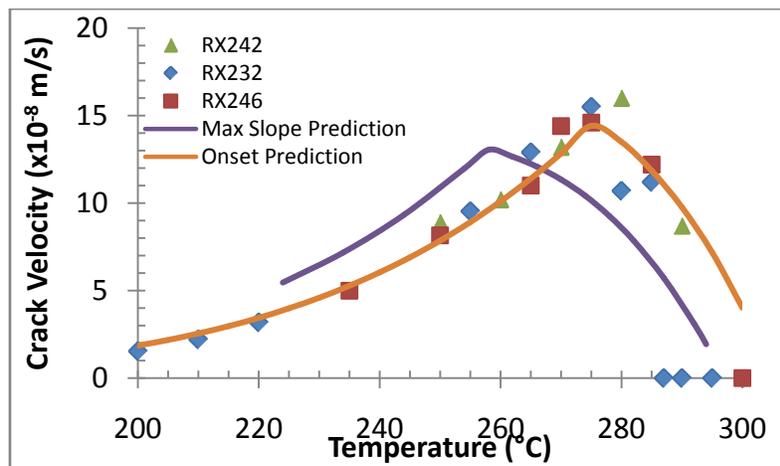


**Figure 3: DHC fracture surfaces showing bulk hydrides in the left image, but none in the right image, which were tested below and above, respectively, the onset temperature (280 °C) and the maximum slope temperature (266 °C)**

The experimental observations showing the peak DHC velocity is coincident with the onset, and that the onset is the demarcation point for hydrides in the bulk are strong arguments for choosing the onset temperature as the precipitation temperature. In addition, predictions with the DFM support the onset temperature as well.

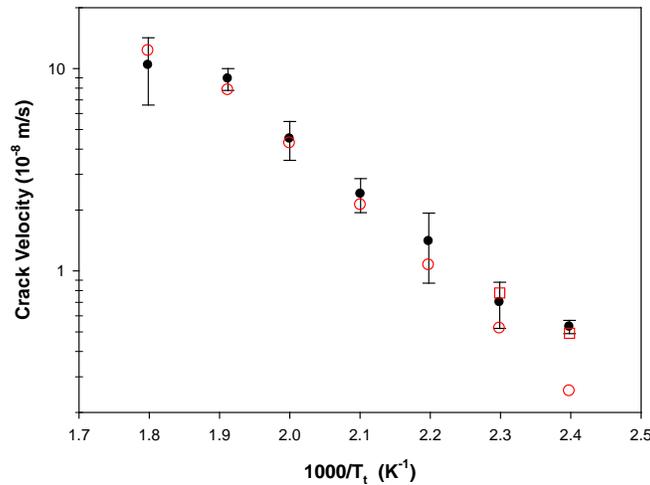
The Diffusion First Model can be used to predict the velocities shown in Figure 1. Two predictions are shown in Figure 4; both are derived using the method described in [1]. The prediction shown by the line labelled 'Max Slope Prediction' in the figure is based on the CSA equation for TSSP [2], which is derived from maximum slope temperatures. The prediction labelled 'Onset Prediction' uses the onset temperature to define TSSP. The details of the onset prediction will be published elsewhere. The improved agreement of the predictions with the observations is mainly caused by shifting the TSSP temperature to the onset temperature.

Establishing an accurate equation for TSSP concentrations in terms of onset temperatures is the subject of current work. An approximate relation is obtained by shifting the temperature in the CSA equation to account for the difference between the maximum slope temperature and onset temperature. This approximate equation can be incorporated into the DFM with the same model parameters used to produce the 'Onset Prediction' of Figure 4, and then used to predict velocities for specimens with different total hydrogen concentrations tested at different temperatures. The goal is to see how well the DFM, with the onset correction, predicts beyond the temperatures and concentration of the current study.



**Figure 4: Longitudinal DHC Crack Velocities as a function of temperature with DFM predictions**

One of the best data sets to test any model of DHC is found in the IAEA 'round-robin' study [3]. Researchers in laboratories from ten countries coordinated to test identically prepared specimens at seven hydrogen concentrations and temperatures. These tests were done above TSSP and below, so they provide a stringent test of any model. The results for cold worked Zr-2.5Nb are shown in Figure 5 along with the predictions from the DFM with the onset temperature correction. The predictions fall within one-standard-deviation of the observations, except for the two lowest temperature points, which may be affected by the delta-to-gamma hydride phase transition, as described in [1].



**Figure 5: Zr-2.5Nb IAEA data. The red circles represent the DFM prediction with the onset correction. The red squares show the result of a further modification to TSSP below 170 °C to account for the delta-to-gamma hydride transition [1].**

#### 4. Concluding Remarks

Experimental observations show the peak DHC velocity is coincident with the onset temperature for precipitation of hydrides, which is defined as the temperature where the DSC curve first begins to change as hydrides precipitate on cooling. In addition, metallography of the fracture surfaces shows that the onset temperature is the demarcation point for hydrides in the bulk, with hydrides present below, but not above this temperature. Predictions with the Diffusion First Model agree well with observations over a wide range of concentrations and temperatures if the TSSP temperature is shifted from the CSA maximum slope value to the onset temperature. Thus, the onset temperature is proposed to be the precipitation temperature to use in studies of DHC.

#### 5. References

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