

# STEADY-STATE MODEL OF DELAYED HYDRIDE CRACKING IN ZIRCONIUM ALLOYS

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## ABSTRACT

The presented model is based on the steady-state solution of diffusion equation and provides the improved description of the acting stress in the process zone ahead of the crack tip, refines the location and critical characteristics of the crack-tip hydride plate. This model allows the prediction of the DHC velocity for the different metallic materials.

The DHC velocity in Zr-2.5Nb reactor pressure tube material was estimated for different hydrogen content. The predicted velocity is governed by the Arrhenius law with activation energy  $\sim 58650$  J/mol. The threshold temperature for the DHC depends on hydrogen content and increases from 205°C (for 25 wt. ppm H) to 305°C (for 100 wt. ppm H). A very good agreement was obtained between predicted results and available experimental data.

## 1 INTRODUCTION

The presence of hydrogen in metals and alloys can result in their localized embrittlement and delayed hydride cracking (DHC). The DHC in zirconium alloys is characterised by an initiation and stable crack growth. The crack initiation and propagation mechanism is controlled by the following processes: diffusion of hydrogen to the region of high stress ahead of the crack tip, hydrogen accumulation and hydride precipitation at the crack tip where hydrostatic stress reaches maximum value, growth of the crack tip hydride to a critical size at which it fractures. The crack propagates through the hydride and the process then repeats again until the crack becomes unstable. The DHC is characterized by the average crack growth rate which is called the DHC velocity. The DHC response is also associated with the threshold stress intensity factor  $K_{IH}$  below which the crack does not grow.

The DHC problem is very important for zirconium alloys widely used in nuclear industry for nuclear plants with high-temperature water environment as a coolant.

In contrast to the experimental observations of the DHC process, there is relatively little progress made in a theoretical analysis of the stable crack propagation. The DHC velocity can be associated with growth of crack tip hydride and, therefore, determined by the rate of hydrogen flux into the highly stressed region ahead of the crack tip. In general, the equation for the DHC velocity follows from the solution of the diffusion equation, assuming steady-state diffusion of hydrogen from surrounding bulk hydrides to the hydride at the crack tip. The theoretical models assume that the crack velocity is equal to the growth rate of the crack tip hydride.

In the case of the DHC, the hydride can be associated with a meso volume or the fracture process volume which is located in the region of stress gradient ahead of the crack tip. The objective of this study is to develop the steady-state model for prediction of the DHC velocity in zirconium based alloys taking into account the stress distribution ahead of the crack tip and the hydride volume (the fracture process volume).

## 2 STRESS STATE IN THE VICINITY OF THE CRACK

The hydrostatic stress ahead of the crack tip is given by the well-known form

$$\hat{\sigma} = \frac{2}{3} \frac{(1+\mu)K_I}{\sqrt{2\pi r}} \cos \frac{\theta}{2}. \quad (1)$$

Here,  $K_I$  is the stress intensity factor (Mode I),  $\mu$  is the Poisson's ratio,  $r$  and  $\theta$  are polar coordinate situated at the crack tip. The hydrostatic stress has maximum on the crack extension line at  $\theta = 0$ . It means that the dissolved hydrogen will be accumulated mainly in the crack plane.

The size of the plastic zone  $r_p$  and corresponding hydrostatic stresses  $\hat{\sigma}_p = \hat{\sigma}(r_p)$  on the crack line extension can be calculated from eqn (1) and von Mises yield criterion

$$r_p = \frac{(1-2\mu)^2}{2\pi} \left( \frac{K_I}{\sigma_y} \right)^2, \quad \hat{\sigma}_p = \frac{2}{3} \frac{(1+\mu)}{(1-2\mu)} \sigma_y, \quad (2)$$

where  $\sigma_y$  is the yield stress of material. In the plastic zone  $r < r_p$  the stresses are not uniformly distributed. The maximum hydrostatic stress  $\hat{\sigma}_m$  occurs at the point  $r_m$  in the plastic zone. It is assumed that the hydrostatic stress is linearly distributed within the regions  $0 \leq r \leq r_m$  and  $r_m \leq r \leq r_p$ . A simple force balance leads to the following estimation (Matvienko [1])

$$\hat{\sigma}_m / \hat{\sigma}_p = 1 + q, \quad q = r_m / r_p. \quad (3)$$

Therefore, the hydrostatic stresses ahead of the crack tip ( $\theta = 0$ ) can be written as follows

$$\hat{\sigma}(r) = \begin{cases} \frac{2}{3} \frac{(1+\mu)K_I}{\sqrt{2\pi r}} & \{r \geq r_p\}, \\ \frac{\hat{\sigma}_p}{1-q} \left( 1 - \frac{qr}{r_p} \right) & \{r_m \leq r < r_p\}, \\ \frac{(1+q)\hat{\sigma}_p r}{qr_p} & \{0 \leq r < r_m\}. \end{cases} \quad (4)$$

Assuming that there is continuity of derivative  $d\hat{\sigma}/dr$  at the point  $r_p$  (Shi [2]), the  $q$ -estimation gives  $q = 1/3$ . Frequently, a simple cylindrical approximation is conservatively applied to describe the stress field in the vicinity of the crack tip (Sagat et. al. [3]).

### 3 THE STEADY-STATE MODEL OF THE DHC PROCESS

The DHC velocity can be associated with growth of crack tip hydride and, therefore, determined by the rate of hydrogen flux into the highly stressed region ahead of the crack tip. The isothermal hydrogen flux in solid solution ( $\alpha$ -phase) is

$$J(r) = -D \left\{ \frac{dc_H(r)}{dr} - \frac{c_H(r)F(r)}{RT} \right\}, \quad (5)$$

where  $F(r) = dW(r)/dr$  is the driving force due to the hydrostatic stresses;  $T$  is the absolute temperature;  $R$  is the gas constant;  $W(r) = \hat{\sigma}(r)\bar{V}$  is molar interaction energy of stress with hydrogen in solution;  $c_H$ ,  $D$ ,  $\bar{V}$  are the concentration, diffusion coefficient of hydrogen in zirconium and partial molar volume of hydrogen in the  $\alpha$ -phase, respectively.

The second Fick's law

$$\frac{dc_H(r)}{dt} = -\frac{1}{r} \times \frac{d\{rJ(r)\}}{dr} \quad (6)$$

and eqn (5) lead to a differential equation for steady-state condition  $\{ dc_H(r)/d\tau = 0 \}$  as follows

$$\frac{dc_H(r)}{dr} - \frac{c_H(r)F(r)}{RT} = \frac{c_1}{rD}. \quad (7)$$

Here  $\tau$  is instantaneous time. A general solution of eqn (7) has the form

$$c_H(r) = \exp\left[\frac{W(r)}{RT}\right] \times \left\{ c_2 + \frac{c_1}{D} \int \frac{1}{r} \exp\left[-\frac{W(r)}{RT}\right] dr \right\}, \quad (8)$$

where  $c_1$  and  $c_2$  are the constants.

One can see that the following expression  $J(r) = -c_1/r$  yields from eqns (5) and (7). To determine the constant  $c_1$ , it is enough to know the concentration  $c_H(r)$  at two points of hydrogen diffusion zone, for example, at  $r = r_0$  and  $r = r_N$ . Substituting these concentrations  $c(r_0)$  and  $c(r_N)$  into eqn 8 gives

$$J(r) = -\frac{D}{Ar} \left\{ c_H(r_N) \exp\left[-\frac{W(r_N)}{RT}\right] - c_H(r_0) \exp\left[-\frac{W(r_0)}{RT}\right] \right\}, \quad (9)$$

where  $A = \int_{r_0}^{r_N} \frac{1}{r} \exp\left[-\frac{W(r)}{RT}\right] dr$ . The well-known trapezium method has been employed to calculate this integral.

As discussed above, the crack-tip hydride is precipitated at the point  $r_m$  where the maximum hydrostatic stresses take place. Hydrogen flux causes the increase of the hydride length  $l$  and thickness  $\psi$ . As a result, specific composite ( $\alpha+\delta$ ) containing the plastic metallic  $\alpha$ -phase and brittle hydride  $\delta$ -phase is formed in the crack plane. When the crack-tip hydride platelet reaches the critical length  $l_c$  and thickness  $\psi_c$ , it fractures. The crack propagates through the embrittled region ( $\alpha+\delta$ ) to be arrested by the ductile  $\alpha$ -phase. The process repeats again, resulting in slow crack growth.

The crack-tip hydride platelet of critical volume  $V_c = l_c \psi_c h$  contains the certain amount of hydrogen:  $n_c = V_c / V_\delta$ , where  $V_\delta$  is the molar volume of the  $\delta$ -phase,  $h$  is height of the hydride. Estimation of the time  $\tau_c$ , which is necessary to form the critical hydride, is based on the hydrogen flux via the boundary  $r_c = r_m + l_c$

$$n_c = \frac{l_c \psi_c h}{V_\delta} = -2\pi r_c h J(r_c) \tau_c. \quad (10)$$

In this case, the DHC velocity is determined as

$$U_{DHC} \approx \frac{r_c}{\tau_c} = -\frac{2\pi J(r_c) \mathcal{W}_\delta \left(\frac{r_c}{l_c}\right)^2}{\beta}, \quad (11)$$

where  $\psi_c / l_c = \beta$ .

To evaluate the hydrogen flux  $J(r_c)$ , it is necessary to know the concentration of hydrogen  $c_H(r_0)$  and  $c_H(r_N)$ . It is supposed that  $r_0 = r_c$  and  $r_N = 20r_p$ . The volume of radius  $r_0 = r_c$  confines the region in which both formation and growth of the  $\delta$ -phase occur. Therefore, the following expression can be written  $c_H(r_0) = c_{TSSP}$ , where  $c_{TSSP}$  is terminal solid solubility for pre-

precipitation (TSSP) of the hydride. The radius  $r_N$  is assumed to be  $20r_p$  and corresponds to the criterion  $F(r_N) = 0,01F(r_p)$  (Shmakov et. al. [4]). In this region hydrogen diffusion is stress affected. The concentration  $c_H(r_N)$  strongly depends on the thermal history of material. For example, if  $c_H^0$  is the hydrogen concentration in the  $\alpha$ -phase at some temperature  $T_0$ , cooling the specimen to the test temperature  $T_{test}$  leads to the following correlation

$$c_H(r_N) = \begin{cases} c_{TSSP}(T_{test}), & c_H^0 > c_{TSSP}(T_{test}), \\ c_H^0, & c_H^0 \leq c_{TSSP}(T_{test}). \end{cases} \quad (12)$$

#### 4 PREDICTION OF THE DHC VELOCITY IN Zr-2.5Nb PRESSURE TUBE MATERIAL

To predict the DHC velocity in Zr-2.5Nb alloy, necessary data were employed from Refs. (Sagat et. al. [3], Shmakov et. al. [4, 5], MacEwen et. al. [6]). The literary data on the terminal solid solubility of hydrogen in zirconium-based reactor alloys with different oxygen content were analyzed in the recent investigation (Shmakov et. al. [4]). It was shown that terminal solid solubility for dissolution (TSSD) data, describing the dissolution solvus  $(\alpha + \delta) \rightarrow \alpha$ , obey the temperature dependence

$$c_{TSSD} \{wt.ppmH\} = (1.26 \pm 0.09) \times 10^5 \exp[-(4350 \pm 50)/T], \\ \{ \{1wt.ppmH \approx 6.45 molH / m^3\} \}. \quad (13)$$

The TSSP data, describing the precipitation solvus  $\alpha \rightarrow (\alpha + \delta)$ , can be estimated from the data on the TSSD:

$$c_{TSSP}(T) = c_{TSSD}(T + \Delta T), \quad (14)$$

where  $\Delta T$  is the temperature hysteresis in the range of 25–75K. Besides, it is known that the terminal solid solubility of hydrogen in zirconium alloys is practically independent on the acting mechanical stress (MacEwen et. al. [6], Shi [7]).

The critical length of the crack-tip hydrides in Zr–2.5Nb pressure tubes of CANDU is approximately equal to 15  $\mu m$  at 423K (Yan and Eadie [8]) and 20  $\mu m$  at 523K (Markelov et. al. [9]). Therefore, assuming that the hydride length  $l_c$  is linear dependent on temperature, the following equation can be obtained

$$l_c \{ \mu m \} = 7.5 + 0.05(T - 273). \quad (15)$$

The steady-state DHC velocity in Zr–2.5Nb material with different hydrogen content (25, 50 and 100 wt. ppm H) was estimated for  $K_I = 20 MPa\sqrt{m}$ . The cooling of the specimens was simulated from the temperature at which all hydrogen was dissolved in the  $\alpha$ -phase. Besides, we supposed the initially uniform hydrogen distribution and the typical temperature hysteresis  $\Delta T = 30K$  (Shmakov et. al. [4]) and  $\beta = 0.1$  (Sagat et. al. [3]). The predicted DHC velocity is presented in Fig. 1.

At low temperatures the predicted DHC velocity is the same for all hydrogen contents. Figure 1 also reveals that the crack velocity exhibits an Arrhenius relationship

$$U_{DHC} \{ m/s \} = 0.064 \exp(-7055/T), \quad (16)$$

with activation energy  $\sim 58650$  J/mol, which is in agreement with the experimental activation energy 56500 J/mol (Singh et. al. [10]) for Zr-2.5Nb alloy. However, the individual temperature threshold

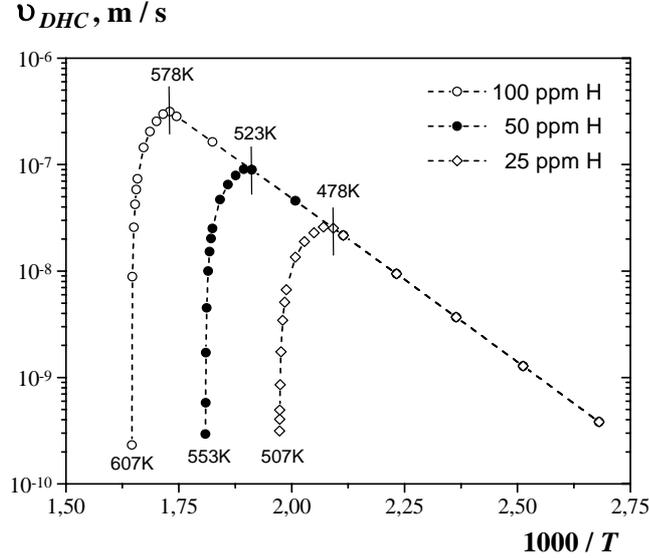


Figure 1: The temperature dependence of the DHC velocity in Zr–2.5Nb alloy for different hydrogen content.

$T_{DHC}$  exists for each composition. At the temperatures  $T > T_{DHC}$  a sharp deviation from eqn (16)

occurs and a DHC process is stopped. The temperature  $T_{DHC}$  increases with the hydrogen content from 205<sup>0</sup>C (for 25 wt. ppm H) to 305<sup>0</sup>C (for 100 wt. ppm H). The obtained results is in agreement with eqn (12). When  $c_H^0 \leq c_{TSSP}$ , the ascending diffusion of hydrogen is necessary to provide the crack tip hydride growth. By other words, the hydrogen diffusion due to the hydrogen concentration gradient must be provided by the acting mechanical stresses. The process is stopped when the applied stress intensity factor becomes insufficient to overcome this gradient.

The predicted DHC velocity is consistent with the experimental results (Markelov et. al. [9], Singh et. al. [10]) performed on standard Zr–2.5Nb reactor pressure tubes (Fig. 2). It can be seen that the theoretical dependence is practically consistent with the experimental points.

## 5 CONCLUSIONS

The model of the DHC process in zirconium alloys has been proposed on the basis of steady-state solution of the phenomenological diffusion equation.

The DHC velocity was estimated in Zr–2.5Nb alloy with different hydrogen content (25, 50 and 100 wt. ppm H). As shown, the predicted velocity obeys the Arrhenius law with activation energy ~58650 J/mol. The threshold temperature for the DHC depends on hydrogen content and increases from 205<sup>0</sup>C (for 25 wt. ppm H) to 305<sup>0</sup>C (for 100 wt. ppm H). A good agreement between the predicted and measured DHC velocities was obtained.

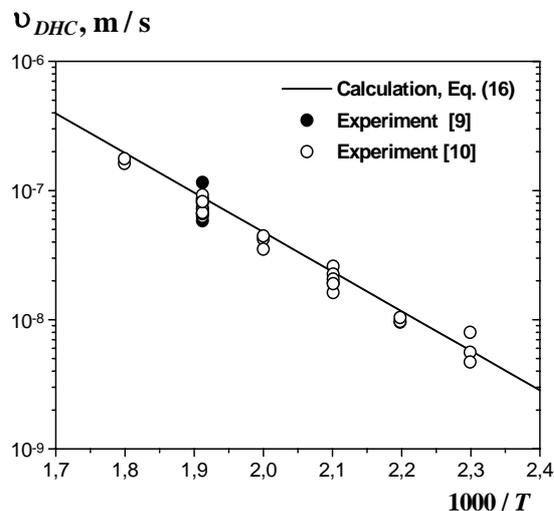


Figure 2: The DHC velocity in Zr–2.5Nb pressure tubes material.

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