A combined SIF and temperature model of delayed hydride cracking in zirconium materials

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Abstract

In the last four decades several theoretical models have been developed to diagnose the DHC velocity in zirconium alloys. However, majority of the known models ignore a dependence of the crack-tip hydrides on stress intensity factor (SIF) and temperature. In this paper we first present the integrated model of DHC which combines two independent calculation models. The first calculation sub-model is designed to predict the critical characteristics of hydrides (their length and thickness) depending on both temperature and SIF. On this basis, the second calculation sub-model allows us to diagnose the DHC velocity. As a whole, the present model is based on the steady-state solution of diffusion equation, provides the improved description of the local stress in the process zone ahead of the crack and refines the location and critical characteristics of the crack-tip hydride platelets. To illustrate the efficacy of our model some of the recent experimental data are presented on DHC in Zr–2.5%Nb pressure tubes used in Canadian and Indian PHWR's (Pressurized Heavy Water Reactors).
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1. Introduction

Dilute zirconium alloys such as the Zircaloys, Zr–1%Nb and Zr–2.5%Nb are widely used in the nuclear industry as the core structural materials of water-cooled nuclear reactors. During their service a part of hydrogen (deuterium) produced through the corrosion reaction of Zr with hot coolant is absorbed by materials. Hydrogen or Deuterium in excess of solid solubility precipitates out as hydride phase of platelet morphology and could make the host matrix brittle. Hydride induced embrittlement significantly influences the in-service performance of the Zr-alloy com-

ponents. Delayed Hydride Cracking (DHC) is a localized form of hydride embrittlement, which is generally accepted as a repeated process which involves stress-induced hydrogen diffusion resulting in its accumulation ahead of the crack, hydride precipitation and fracturing of the brittle hydrided region. The DHC velocity dependence on the mode-I stress intensity factor K_1 is shown schematically in Fig. 1. The condition for crack growth is $K_1 \geqslant K_{1H}$, where K_{1H} is the threshold stress intensity factor for DHC. As is well known [1], the DHC velocity is very sensitive to K_1 in stage I and nearly constant in stage II up to the fracture toughness of material K_{1C}.

The first incident connected with DHC in Zr–2.5%Nb reactor pressure tubes was observed in the 1970s. After that extensive research on DHC in zirconium-based commercial alloys has been carried out. In particular, only in the last

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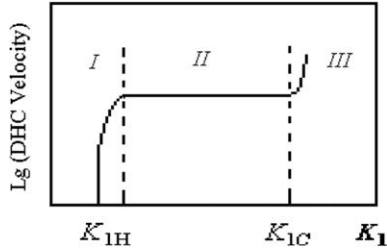 *E-mail address:* Ram.Singh@ts.mah.se (R.N. Singh).

Fig. 1. The DHC velocity vs. stress intensity factor.

decade a number of theoretical models (e.g. [2–7]) were proposed to predict the basic parameters of DHC such as the stable crack growth velocity and K_{1H}. Unfortunately, most of the known models ignore the dependence of the crack-tip hydrides on temperature and K_1. Such presumption essentially reduces the reliability of theoretical predictions. In this paper, we present a DHC model based on the steady-state solution of diffusion equation. The proposed model provides the improved description of the local stress in the process zone ahead of the crack, refines the location and critical characteristics of the crack-tip hydride plate. Finally some of the recent experimental data on DHC velocity in Zr–2.5%Nb pressure tubes used in Canadian and Indian PHWR's (Pressurized Heavy Water Reactors) are compared with the values predicted by the proposed model.

2. Two phase composite model of DHC based on elastic fracture mechanics

A distribution of tensile stresses σ on the crack-tip extension line is shown in Fig. 2. The plastic zone size is given under plane strain by the known equation

$$r_P = \frac{(1 - 2v)^2}{2\pi} \left(\frac{K_1}{\sigma_{YS}}\right)^2 \tag{1}$$

where v is the Poisson's ratio; σ_{YS} is the yield strength of material. In the elastic zone ahead of the crack ($r > r_P$) the normal tensile component σ_y and hydrostatic stress $\hat{\sigma}$ are

$$\sigma_y(r) = \frac{K_1}{(2\pi r)^{1/2}}; \quad \hat{\sigma}(r) = \frac{2(1 + v)K_1}{3(2\pi r)^{1/2}}. \tag{2}$$

From the concept of force balance and assuming a linear distribution of stresses in the plastic zone regions $0 \leqslant r \leqslant r_M$ and $r_M \leqslant r \leqslant r_P$, one can write [4]:
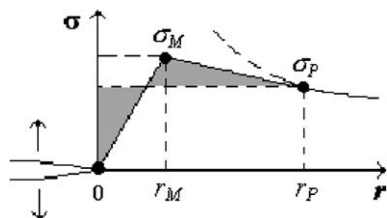

Fig. 2. The tensile stresses ahead of the crack tip.

$$\frac{\sigma_M}{\sigma_P} = 1 + \frac{r_M}{r_P} = 1 + q, \tag{3}$$

where $\sigma_P = \sigma(r_P)$, r_M is the position of maximum stress, σ_M. From Eqs. (1) to (3) and assuming a continuity of the derivative $d\sigma/dr$ at the elastic-plastic boundary $r = r_P$ one can obtain $q = 1/3$ [7].

It is known that hydrogen in solid solution accumulates in the regions with the highest tensile stresses. When the hydrogen concentration in such regions exceeds the terminal solid solubility for precipitation of hydrides (TSSP), the brittle hydride platelets form normal to the major stress. It may be noted that the microstructure and texture of the fabricated zirconium alloy tubes for reactor application are such that mainly circumferential hydrides precipitate out in the absence of external load [8]. However, only radial hydrides cause the DHC process in axial or radial direction of the tube. Therefore, the stress-oriented hydride platelets must precipitate out of solid solution in the crack plane. Thus, we can suppose that radial hydrides at the crack-tip must precipitate firstly at the point r_M (Fig. 2). Stress induced hydrogen diffusion towards the crack-tip region causes an increase of the hydride length and thickness. As a result, $\alpha + \delta$ region containing the plastic metallic α-phase and brittle hydride δ-phase is formed in the crack plane. It is expected to locally reduce the fracture toughness of material. When the crack-tip hydride reaches its critical length l_C the fracture toughness of material is reduced to the level of the applied stress intensity factor K_1. The crack propagates through the embrittled region $\alpha + \delta$ up to the point $r_C = r_M + l_C$ to be arrested by the ductile α-phase (Fig. 3). This process called DHC is repeated in a step-by-step manner, resulting in slow crack growth. For the two phase region ahead of crack tip comprising of α- and δ-phases weighted superposition, yields

$$K_1 = W_\alpha K_{1C}^\alpha + W_\delta K_{1C}^\delta = \frac{r_M}{r_M + l_C} K_{1C}^\alpha + \frac{l_C}{r_M + l_C} K_{1C}^\delta \tag{4}$$

where W_α and W_δ are the fractions of the α- and δ-phases in the cracked composite $\alpha + \delta$; K_{1C}^α and K_{1C}^δ are the fracture toughness of the α- and δ-phases, respectively. It is evident from Eq. (4) that W_α and W_δ are geometry dependent. The fracture toughness criterion described by Eq. (4) results in the relation [9]
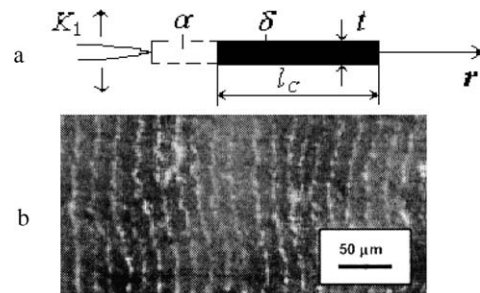

Fig. 3. The location of the hydride platelet before cracking (a) and striations observed in Ref. [10] on fracture surface during DHC (b).

$$l_C = \frac{(1-2v)^2}{6\pi}\left(\frac{K_{1C}^{\alpha} - K_1}{K_1 - K_{1C}^{\delta}}\right)\left(\frac{K_1}{\sigma_{YS}}\right)^2 \qquad (5)$$

from which the critical length l_C increases infinitely at $K_1 = K_{1C}^{\delta}$ and reduces to zero at $K_1 = K_{1C}^{\alpha}$. Besides, owing to the ductile α-phase layer, separating the crack and crack-tip hydride platelet (Fig. 3), the threshold factor K_{1H} will be always larger than K_{1C}^{δ}.

Due to the very large (17%) volume increase associated with the $\alpha \rightarrow \delta$ transformation, the δ-hydride platelet formed in the matrix α-phase is expected to be compressed if no external stress is applied. The fracture toughness of the compressed hydrides was estimated in the present investigation using a calculation scheme reported in literature [2–4] assuming plane strain case. In general case, the effective stress in such hydride is the sum of an externally applied stress σ_y with no hydride present and a stress σ_δ generated by the hydride formation process in the absence of external load. It is assumed that the hydride cracks when the effective stress, acting normal to the crack plane, exceeds the hydride fracture strength σ_F. If the compressive stresses are not significantly relaxed and $r > 0.25t$, they are suggested to be of the form [2,3]

$$\sigma_\delta(r) = -\frac{E\varepsilon_\perp}{4\pi(1-v^2)}\left(\frac{t}{r}\right) \qquad (6)$$

where E is the Young's modulus; $\varepsilon_\perp$ is the stress free strain in direction normal to the formed hydride platelet; t is the hydride thickness. According to Eqs. (1)–(3), the location and value of the maximum tensile stress can be estimated for $K_1 = K_{1C}^{\delta}$ as follows:

$$r_M = \frac{(1-2v)^2}{6\pi}\left(\frac{K_{1C}^{\delta}}{\sigma_{YS}}\right)^2; \quad \sigma_y(r_M) = \frac{4\sigma_{YS}}{3(1-2v)} \qquad (7)$$

Eqs. (6) and (7) allow us to write a fracture criterion $\sigma_y(r_M) + \sigma_\delta(r_M) = \sigma_F$ and estimate the fracture toughness of the infinitely long compressed hydride in the form [4,9]:

$$(K_{1C}^{\delta})^2 = \frac{9E\varepsilon_\perp t(\sigma_{YS})^2}{2(1-v^2)(1-2v)[4\sigma_{YS} - 3(1-2v)\sigma_F]}. \qquad (8)$$

3. Discussion

3.1. Critical dimension of crack-tip hydrides

An experimental study of the first crack-tip hydrides forming during DHC in Zr–2.5%Nb pressure tubes of CANDU nuclear reactors was recently conducted [5,11]. The obtained experimental points are shown by symbols in Fig. 4. Using the data in Fig. 4 and Table 1, from Eq. (5) we can estimate a fracture toughness of the α and δ phases as $K_{1C}^{\alpha} = 45$ MPa m$^{1/2}$ and $K_{1C}^{\delta} = 5.35$ MPa m$^{1/2}$, respectively. Assuming that the estimated values are nearly invariable in the range of 423–573 K, the temperature dependence of the critical hydride length and thickness
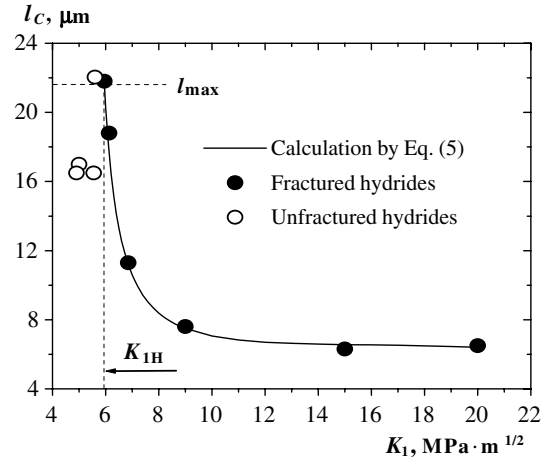

Fig. 4. The first crack-tip hydrides during DHC in Zr–2.5%Nb CANDU pressure tube at 423 K.

Table 1
Parameters of Zr–2.5%Nb pressure tube material

σ_{YS} (MPa) = 1088 − 1.02T	[2,3]
E (MPa) = 111,570 − 57.4T	[2,3]
σ_F (MPa) = 676 − 0.09T	[12]
$v = 0.5 - 3.215 \times 10^{-4}$T	[13]
$\varepsilon_\perp = 0.055$	[13]

can be established using Eqs. (5) and (8). The predicted values are shown in Fig. 5.

3.2. Steady state model of DHC

The crack-tip hydride plate will form at the point of maximum tensile stress and will grow to the size l_C for the fracture criteria to be satisfied. Assuming a cylindrically symmetric stress field with axis of symmetry parallel to the crack front it is suggested that the DHC velocity is controlled by the hydrogen diffusion flux via the critical boundary $r_C = r_M + l_C$ (Fig. 6). Eq. (9) describes the hydrogen flux as a function of distance from crack tip, temperature, dissolved hydrogen concentration and partial molar energies for hydrogen dissolution under hydrostatic stress [7]:

$$J_H(r) = -\frac{D_H}{Ar}\left\{c_H(r_E)\exp\left[-\frac{W_H(r_E)}{RT}\right] - c_{TSSP}\exp\left[-\frac{W_H(r_C)}{RT}\right]\right\},$$

$$A = \int_{r_C}^{r_E}\frac{1}{r}\exp\left[-\frac{W_H(r)}{RT}\right]dr, \qquad (9)$$

where partial molar interaction energy, $W_H(r) = \hat{\sigma}(r)\overline{V}_H$, with $\overline{V}_H = 1.67 \times 10^{-6}$ m^3/molH = partial molar volume of hydrogen in solution; $c_H(r)$ = hydrogen concentration in solution; $D_H\{m^2/s\} = 2.9 \times 10^{-7}\exp(-38,080/RT)$ = hydrogen diffusion coefficients. The boundary of hydrogen diffusion zone may be estimated as $r_E = 20r_P$ [6]. The hydrogen precipitation solvus for Zr–2.5%Nb alloy, $c_{TSSP}\{molH/m^3\} = 8.514 \times 10^5\exp(-36,300/R[T + \Delta T])$ where ΔT = hysteresis
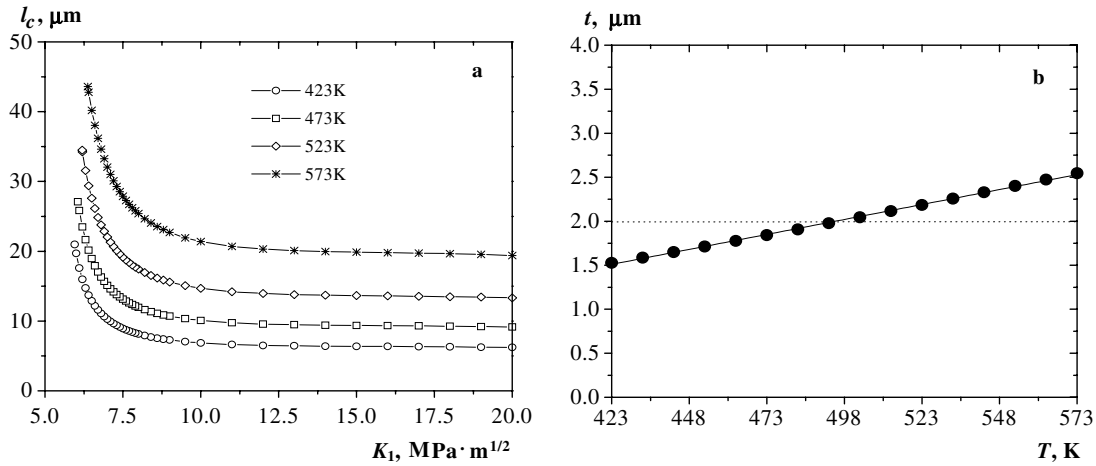
Fig. 5. The calculated characteristics of the first crack-tip hydrides: (a) critical length; (b) thickness.
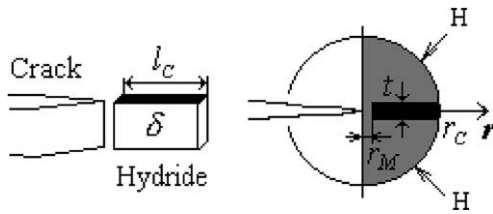

Fig. 6. Illustration of cylindrically symmetric stress field ahead of the crack tip. The region of hydrogen accumulation is shaded.

of hydrogen terminal solid solubility and has been assumed in the present calculation to be 50 K. The hydrogen concentration $c_H(r_E)$ depends on the thermal history of material and can be expressed as

$$c_H(r_E) = \begin{cases} c_{TSSP}(T_{test}), & c_H^0 > c_{TSSP}(T_{test}); \\ c_H^0, & c_H^0 \leqslant c_{TSSP}(T_{test}), \end{cases} \quad (10)$$

where c_H^0 is the hydrogen concentration in solution at some temperature $T_0 > T_{test}$. The amount of hydrogen in hydride platelets of critical size is equal to $n_C = V_C/V_\delta$, where $V_\delta = 10.9 \times 10^{-6}$ m³/molH is the molar volume of the δ-hydride phase. The time which is necessary to form the critical hydride is

$$\tau_C = -\frac{t l_C}{\pi r_C J_H(r_C) V_\delta}, \text{ which implies that } \upsilon_{DHC} \approx \frac{r_C}{\tau_C}$$

$$= -\frac{\pi (r_M + l_C)^2 V_\delta J_H(r_C)}{t l_C}. \quad (11)$$

The calculation of the DHC velocity in Zr–2.5%Nb pressure tube material was performed for $K_1 = 20$ MPa × m$^{1/2}$ using Eq. (11) and estimated values $l_C\{\mu m\} = 0.26 \exp(7.58 \times 10^{-3} T)$ and $t = 2$ μm. The obtained theoretical dependence is

$$\upsilon_{DHC}\{m/s\} = 0.033 \exp(-56,700/RT). \quad (12)$$

An experimental velocity of DHC was recently measured in gaseously charged up to 40–80 wt. ppm H standard Zr–2.5%Nb pressure tubes of Indian and Canadian PHWRs
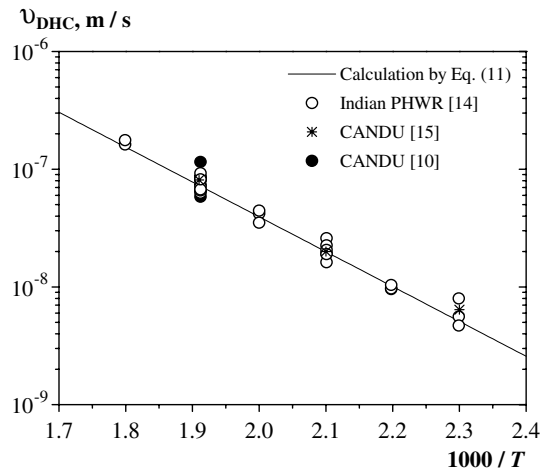

Fig. 7. Comparison of theoretically predicted DHC velocity with the experimentally observed values for Zr–2.5%Nb pressure tube alloys.

[10,14,15]. The isothermal DHC tests were carried out using curved compact tension specimens (17 mm wide) having a fatigue crack along the radial–axial plane of the tube. The specimens were heated up to the peak temperature at which all hydrogen must be dissolved in the α-phase. After some annealing the specimens were slowly cooled to the test temperature. The propagation of the crack was monitored by the electric potential drop method. The theoretically predicted and experimental values of DHC are compared in Fig. 7. As is evident, a very good mutual agreement between experimental and theoretical data was obtained.

4. Conclusions

The combined SIF and temperature model of DHC is developed. This model combines two independent calculation models. The first calculation sub-model is designed to predict the critical characteristics of hydrides (their length and thickness) depending on both temperature and stress

intensity factor. On this basis, the second calculation sub-model allows us to prognosticate the DHC velocity. It is shown, that theoretical results predicted for Indian and Canadian Zr–2.5%Nb PHWR pressure tubes are consistent with the measured values.

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