

DEVELOPMENTS IN DELAYED HYDRIDE CRACKING IN ZIRCONIUM ALLOYS

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ABSTRACT

Delayed Hydride Cracking is a process of diffusion assisted hydride embrittlement at flaws. DHC Models of DHC propagation and initiation have been developed that capture the essential elements of this phenomenon in terms of parameters describing processes occurring at the microscale. The models and their predictions of experimental results are assessed. No models have yet been developed that combine DHC initiation and propagation. Although the models are capable of describing the essential features of DHC, all of them are highly idealized and in need of further refinement.

1 INTRODUCTION

Zirconium alloy components can fail by a time-dependent mechanism of cracking if they contain hydrides, sharp flaws and are sufficiently stressed. The mechanism of time-dependent hydride cracking, called Delayed Hydride Cracking (DHC), is based on diffusion of hydrogen to the flaw tip, followed by nucleation, growth, and fracture of the flaw-tip hydride. By repeating these processes, a crack can propagate through the component at a rate that, above a threshold stress intensity factor K_{IH} , is mainly dependent on temperature. In this paper we present the status of our state of understanding of DHC in zirconium alloys emphasizing the models developed and their experimental verification. The paper is divided into two parts one part dealing with DHC propagation, and the other part dealing with hydride crack initiation.

2 DHC PROPAGATION

The first model of DHC propagation was developed by Dutton and Puls [1]. Subsequent comparison with early experimental data showed good agreement with the temperature dependence of the DHC velocity and reasonable agreement with its dependence on K_I (Dutton et al [2] and Simpson and Puls [3]). The original version of the model [1,2] did not account for the hysteresis in the solvus, which has important effects on the temperature dependence of the DHC velocity, which was shown by Simpson and Puls [3] and Ambler [4] as depending on the direction of approach above a certain temperature. This was incorporated by Puls [3] based on a theoretical analysis of the solvus [5]. Further advances in the model focussed on improvements in experimental (see for example Pan et al [6]) and theoretical (Puls [7,8]) understanding of the solvus. The most recent update of the steady state model is discussed by Puls [9]. Sagat et al [10] show how the model is modified to account for the case when there is a temperature gradient from the crack tip to the bulk of the material. The isothermal model is discussed in the following in terms of its applications to Zr-2.5Nb pressure tube material used in CANDU™ reactors (CANDU is a trademark of Atomic Energy of Canada Ltd). Assuming cylindrical geometry, the model calculates the steady state growth of a hydride formed at a crack tip at $r = \ell$ fed by hydrides in the

bulk at $r = L$. The expression for the DHC velocity, dc/dt , where c is the crack length and t is time is given by [9]:

$$dc/dt = (2\pi D_H) / (\Omega_{Zr} \cdot \Phi(L, \ell) \cdot t_{hyd} \cdot N_H \cdot x) \cdot [E_L - E_\ell] \quad (1)$$

where

$$E_L = c_H^{heat} \exp(\bar{w}_t^a(L) / (x \cdot R \cdot T)) \quad (2)$$

$$E_\ell = c_H^{cool} \exp(\bar{w}_t^a(\ell) / (x \cdot R \cdot T)) \quad (3)$$

and

$$\bar{w}_t^a = -\bar{V}_{Zr} \sigma_{ij}^a e_{ij}^T \quad (4)$$

and where \bar{V}_{Zr} = partial molar volume of zirconium and all other parameters are given in [1,2,9].

The solvus concentration c_H^{heat} represents the solubility of hydrogen in equilibrium with hydrides that are in a dissolving state. The solvus concentration c_H^{cool} represents the solubility of hydrogen in equilibrium with hydrides that are in a precipitating mode. In the zirconium literature these two solvi are referred to, respectively, as Terminal Solid Solubility for hydride Dissolution (TSSD) and Terminal Solid Solubility for hydride Precipitation (TSSP) [6]. There is a large hysteresis between these two solvi [6]. Moreover TSSP depends sensitively on prior specimen history and cooling rate while TSSD is little affected by these factors [6]. The upper and lower bounds over which TSSP ranges are denoted by TSSP1 and TSSP2, respectively. These bounds were conjectured by Pan et al [6] to correspond to the solvi relevant to hydride nucleation and growth, respectively.

Eqn (1) shows that there would be no crack growth if $E_L \leq E_\ell$. Experimentally, over the small concentration/temperature range that measurements are made, the solubility has the form

$$c_H^i \approx Cst \cdot \exp(-\Delta G_{sol}^i / (R \cdot T)) \quad (5)$$

where $i = \text{heat or cool}$ and ΔG_{sol}^i is a temperature independent positive value with $-\Delta G_{sol}^{heat} < -\Delta G_{sol}^{cool}$. Therefore, in the bulk, $c_H^{heat} < c_H^{cool}$. At the crack tip, at low temperatures, the interaction energy, $w_t^a(\ell)$, is sufficiently more negative than $w_t^a(L)$ to offset the difference between $-\Delta G_{sol}^{heat}$ and $-\Delta G_{sol}^{cool}$. Therefore, below a certain temperature, $E_L > E_\ell$ and the equation predicts that DHC propagation can occur. The temperature dependence of $w_t^a(\ell)$ arises because the applied stresses on the crack tip hydride are in the plastic zone, and are a multiple of the yield stress, which decreases with temperature. Therefore, above a certain temperature the interaction energy can no longer offset the difference in the hysteresis between TSSD and TSSP (c_H^{heat} and c_H^{cool} , respectively) and the model predicts that DHC cannot occur. The experimental conditions that result in the solvus at L being determined by c_H^{heat} (TSSD) is that the test temperature is approached from below. Experimentally it is found that above about 200°C [4] DHC propagation cannot be induced in Zr-2.5Nb pressure tube material when the temperature is approached from below. However, when the temperature is approached from above and the material contains sufficient hydrogen, DHC propagation is possible up to temperatures at which the fracture limit of hydride under triaxial stresses is reached. This appears to be above around 320°C (Eadie and Smith [11], Sagat and Puls [12]). Eqn (1) can be used to rationalize the foregoing, although the form of the solution would change slightly since the assumption of a fixed hydrogen concentration at L, with the hydrides being the source of hydrogen in solution, would no longer be valid. By approaching the temperature from above and provided that there is enough hydrogen so hydrides are being precipitated at the test temperature, E_L in eqn (1) becomes

$$E_L = c_H^{cool} \exp(\bar{w}_t^a(L)/(x \cdot R \cdot T)) \quad (6)$$

There is thus no longer any hysteresis between the solvi at L and ℓ and, since $w_t^a(\ell) < w_t^a(L)$, eqn (1) predicts that DHC propagation is possible up to the temperature where the stress in the plastic zone at the crack tip would no longer be able to fracture the hydride.

The model predicts that the DHC velocity has an Arrhenius dependence on temperature with the activation energy given largely by the sum of the formation and activation energies, respectively, for hydride formation and hydrogen diffusion. This predicts that the overall activation energy for DHC velocity ranges from 55 to 65 kJ/mol H. Simpson and Puls [3] obtained an activation energy of 65 kJ/mol H for hydrided material but a smaller value for as received material. The difference could be the effect of the state of the beta phase on the effective diffusion coefficient. Zr-2.5Nb pressure tube material consists of flattened alpha phase Zr crystals which are much longer in the tube's axial compared to its transverse direction and which are surrounded by a thin grain boundary network of metastable beta phase of initial composition of Zr-20Nb. This network decomposes with time and temperature such as when hydrogen is added gaseously to the material at 400°C, as was the case in [3]. The beta phase increases its Nb content and loses its continuity. The beta phase has a higher solubility for hydrogen and allows for faster diffusion than the alpha phase. Therefore an alloy with its metastable beta phase intact has a higher effective diffusion coefficient than one where the beta phase has been degraded. In addition the network is geometrically different depending on whether the predominant diffusion path is in the radial or the axial tube direction. Skinner and Dutton [13] took account of these effects and showed how eqn (1) should be modified to account for modifications to the alpha/beta morphology and the direction of propagation. Skinner and Dutton [13] found, for instance, that the activation energy for hydrogen diffusion in as extruded Zr-2.5Nb is less than half that in alpha phase Zr. Based on the difference in the diffusion coefficient, they also found that the radial velocity would be 0.73 lower than the axial velocity, which is in approximate accord with experimental observations of Sagat et al [14]. Experimentally the activation energy for DHC propagation varied from 72 kJ/mol to ~42 kJ/mol [14], which reflects the influence of the alpha/beta phase morphology and crack growth direction on the diffusion coefficient and, hence, the DHC propagation.

The model cannot provide the full dependence of the DHC velocity on K_I since it does not contain a fracture criterion and is a steady state solution. Experimentally [3], it is found that there is a very sharp threshold over which the velocity decreases sharply with K_I (designated stage I) and the K_I value at which the velocity is effectively zero is defined as K_{IH} . Above this value the DHC velocity is practically independent of K_I (designated stage II) until it approaches the fracture toughness limit of the hydride free material where there is a sharp increase. Assuming that in stage II hydride growth, before fracture, is confined to the plastic zone, the model predicts that the K_I -dependence of the velocity in this stage is small [2,9]. A more refined model requires a non-steady state solution, discussed in the following.

Using a finite element technique to obtain diffusion solutions, Metzger and Sauvé [15] and Sofronis and Lugano [16] show how the hydride density is distributed around the crack tip in response to the hydrostatic stress diffusion gradient and how the hydride distribution alters the crack tip stresses through the hydride-matrix misfit strains. The normal tensile stress decreases as the hydride density increases in this direction. In these models [15,16] the hydrides precipitate as a fine cloud in the form of a density distribution. This is then compacted to form a fully dense hydride of the same shape. The shape of this hydride is driven by the diffusional requirement of equi-hydrostatic stress contours. The models predict that the hydride cluster is tapered with the thicker end at the crack tip. This corresponds to observations by Shek [17] and others [2,15], but not in all cases. In reality hydrides form as fully dense platelets that may or may not be distributed

by the dictates of equi-hydrostatic stress contours. Ellyin and Wu [18] show how the stress distribution inside the hydride and at its edges is altered when the hydride forms as a single plate. This calculation shows that there are dramatic variations in stress along the length of the hydride, with some region, away from the crack tip, still under compressive stress if the hydride is thick enough. Note that the calculation shows that at the tip of the hydride, away from the crack tip, there is a peak in tensile stress that would provide a driving force for extension of the hydride platelet.

In contrast to the finite element methods, a less sophisticated, cylindrically symmetric, non-steady state DHC hydride growth model was solved numerically by Shi et al [19]. In this model, the DHC velocity is defined as the ratio of the critical hydride length to the total time required to grow such a hydride. Calculations of the DHC velocity versus K_I show a sharp threshold, defining K_{IH} and stage I. In stage II, the model still gives a gradual decrease of the DHC velocity with K_I as did the steady-state model. Effects of hydrogen concentration, yield stress and temperature on DHC velocity have also been studied using this model [19].

3 DHC INITIATION

Experimental studies by Simpson [20], Puls [21, 22], Choubey and Puls [23] on Zr alloys to determine the conditions required to fracture hydrides, suggested crack initiation models based on a critical stress criterion. In these models it is assumed that the hydrides would fracture only if the local tensile stress at the hydrides is higher than a critical value. Shi and Puls [24, 25] quantified this idea by applying elastic inclusion theory to describe the stress field associated with a three dimensional hydride and then to super-impose this stress field with the externally applied stress field to find the local stress inside the hydride. By using this method, Shi and co-workers [24- 26] have been able to establish quantitative models for K_{IH} and for the critical hydride size for DHC initiation at flaws. Smith [27, 28] used the solution for the stress field of a super-dislocation to represent the stress field produced by a two-dimensional hydride disc, and obtained similar results. The benefits of these stress models are that the results are relatively simple and the physical relationships between various material parameters are quite transparent.

When the stress condition is applied to blunt flaws, the results can be too conservative for flaws with very small root radii and/or flaws that have sharp, short secondary flaws along their bottoms where very high tensile stresses could be achieved, but which would range over only very short distances. In these cases an additional condition is required. Scarth and Smith [29] developed an engineering process zone model, which is an adaptation of the Bilby-Cottrell-Swinden (BCS) Mode III model of crack tip plasticity, to the case of Mode I hydride crack initiation at blunt flaws. This model has two explicit conditions for fracture that must be simultaneously satisfied. One is similar to the foregoing condition that the normal tensile stress in the flaw tip region, p_H , must exceed a critical value, p_c , which is the fracture stress of an infinitely long hydride platelet grown at a smooth surface. The other is that the crack tip opening displacement, v_T , must equal a critical value, $v_c = K_{IH}^2 / (E' \cdot p_c)$ where $E' = E/(1-\nu^2)$, E is Young's modulus and ν is Poisson's ratio of the zirconium alloy matrix material. Conditions regarding the possibility of hydride formation and growth to a sufficient length are implicit in the model. The process zone is the hydrided region along the crack plane over which, in analogy with the BCS model, a constant stress, p_H , is assumed to act. This zone will fracture when $p_H \geq p_c$. The results of Metzger and Sauvé [15] provide a physical justification for this constant-stress assumption, but only if the hydride at the crack tip were, in reality, to distribute itself as a hydride density distribution. When more realistic shapes for hydrides are assumed, then results such as those by Ellyin and Wu [18] show that the stress is anything but uniform. Despite these deficiencies,

comparisons with experiments show that the model provides an adequate lower bound for DHC initiation as a function of the flaw's root radius (Scarth and Smith [29]).

Based only on the critical stress criterion, Shi and Puls [24, 25] derive values for the critical hydride length for fracture at a crack and blunt flaw. For a crack, a lower-bound value for K_{IH} , is obtained for the case when L_c becomes infinitely long [24]. This equation shows that increasing the yield stress of the material would decrease K_{IH} . This is consistent with experimental results [15]. Also a higher K_{IH} is expected for a thicker hydride platelet. This result suggests that microstructures or textures that favour globular hydrides over thin platelets at the flaw tip would result in higher K_{IH} values. Another important conclusion from this equation is that in zirconium alloys, since the yield strength decreases faster than the hydride fracture strength with increase in temperature [30], then the hydride fracture strength σ_f^h will be larger than $\sigma_{ys}/(1-\nu^2)$ (\approx maximum normal tensile stress at the crack tip), which means that DHC will not be possible at high enough temperatures even if massive hydrides were to be present in the matrix and at the crack tip. Such a result has been observed by Smith and Eadie [11] and Sagat and Puls [12]. Subsequent to the Shi and Puls model for K_{IH} , Wäppling et al [31] and Kim et al [32] also developed alternate models.

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