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Review

Review of the thermodynamic basis for models of delayed hydride cracking rate in zirconium alloys

Manfred P. Puls *

MPP Consulting Oakville, ON, Canada L6J 1V7

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A B S T R A C T

A review is given of the thermodynamic basis of a model developed by Dutton and Puls for the rate of subcritical crack propagation by delayed hydride cracking in zirconium alloys. This review was prompted, in part, by the publications of a series of recent papers by Kim and co-workers in which it is claimed that the thermodynamic basis of the Dutton and Puls model and its subsequent refinements is incorrect, prompting them to propose a new model. This review demonstrates the validity of the original model and shows the origin of the error made by Kim in claiming that the Dutton and Puls model was incorrectly formulated. It also explains the reasons why Kim's new delayed hydride cracking model is incorrect. This review was further prompted by the author's realization that the series of papers documenting the development of the various versions of the original Dutton and Puls model contain typographical errors, differences in sign convention, differences in input data, minor errors and/or changes in formal representation as well as occasional misleading, confusing or incorrect statements of the physical significance of the thermodynamic basis of the model. All of these shortcomings could have resulted in misunderstandings regarding the correct formulation of the model and the physical significance of the results. Therefore another important purpose of this review is to provide an updated treatment of the original version that puts all subsequent versions of the DHC model on a consistent thermodynamic basis.

Contents

1. Introduction

Over the last five years, Kim and co-workers have published a series of papers [1–6] the chief aims of which have been to promote a new model for Delayed Hydride Crack (DHC) propagation developed by Kim. The development of this new model was motivated by Kim's perception that the old model (as he called it and as we will refer to it subsequently) was incapable of predicting important aspects of the experimentally observed behaviour of DHC propagation and must have, therefore, been formulated incorrectly. The first version of the old model was developed by Dutton

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* Tel.: +1 905 844 3973.
E-mail address: mpuls@cogeco.ca

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and Puls [7] and was an attempt to mathematically describe, for the first time, the essential features governing what was at that time the newly discovered mechanism of subcritical crack propagation by DHC. Subsequent refinements of this model by Puls [8–10] focussed mainly on incorporating an improved theoretical formulation for the terminal solubility for hydride precipitation and dissolution [9,11,12] without this changing the underlying thermodynamic basis of the model. It was evident to this author when first presented with Kim's views on the old model that Kim's criticism of the old model was unfounded and that, in fact, it was Kim's new model that is incorrect. However, no published account expressing the reason for these conclusions was initially offered. Due to the large number of papers that have since been published by Kim and co-workers that continually repeat these erroneous views concerning the old model and promote his new one, the author feels that it is important to place in the public record his reasons why he thinks Kim's views and his alternate DHC model are incorrect.

One of the earliest publications in an international journal of Kim's rationale and ideas for his new DHC model appeared in [1]. In this paper Kim stated three perceived shortcomings of the old DHC model. The shortcomings were that the model cannot explain, (i) why the magnitude of the DHC velocity is independent of the applied stress intensity factor, (ii) why DHC has a strong dependence on direction of approach to test temperature and (iii) why there is an effect of hydride size on DHC velocity. These perceived shortcomings led Kim to conclude that the key mechanism that is the cornerstone of the old DHC model developed by Dutton and Puls, which is the effect of stress on the chemical potential of diffusion of hydrogen in the lattice of zirconium, cannot be correct or important (it is not clear which he means) and led him to propose a new model that does not depend on this mechanism as the cause of DHC.

It is the purpose of this publication to demonstrate, (i) that the shortcomings given by Kim of the old model are not true and, (ii) that the alternate mechanism proposed by him, which is based on the driving force for DHC being the hydrogen concentration gradient produced as a result of the lowering of the solvus by stress at the crack tip, is not correct. It should be noted that Kim never actually provides a mathematical formulation of his model. This means that no analytic expression for DHC propagation rate was derived nor does he present alternate expressions for the chemical potentials governing hydrogen diffusion and phase equilibrium conditions. The model is essentially presented in qualitative terms, supported by graphical determinations of concentration differences derived from solvus data. This approach leads to some uncertainty in understanding what the physical basis of Kim's model actually is and what quantitative predictions can be obtained with it.

In addressing Kim's points concerning the shortcomings of the various versions of the old model and noting, over the years, the misunderstandings expressed by others, either privately or in open literature or internal publications, concerning the physical interpretation implicit in the thermodynamic formulation of the old model, it had become evident to the author that a review of the various features of the model as progressively modified would be useful. Moreover, it is likely that some of the misunderstandings concerning the old model have arisen because the series of papers documenting the development of the various versions of the old model contain typographical errors, differences in sign convention, differences in input data, minor errors and/or changes in formal representation as well as occasional misleading, confusing or incorrect statements of the physical significance of the thermodynamic basis of the model. The second purpose of this paper, therefore, is to point out and correct these inadequacies in the publication record.

In the following we start by giving a brief summary of the experimentally observed physical features of DHC propagation, followed by a review of the thermodynamic basis of the old DHC model developed to rationalize this phenomenon. This is followed by a description and critique of Kim's new DHC model including addressing his criticisms of the old DHC model. It is shown that Kim has incorrectly interpreted the thermodynamic basis of the old model as well as some of the predictions that were made on the basis of this model, while proposing a new model that variously neglects or incorrectly formulates important terms controlling the thermodynamics of phase equilibrium and diffusion in the Zr–H system. Furthermore, it will also be shown that some of the experimental results cited by Kim in support of his DHC model were erroneously interpreted.

2. Explanation of terminology

It is useful to provide a summary of the terminology used in the remainder of the paper to avoid repeated explanation of their meaning in the rest of the paper.

The focus of this paper is on crack propagation (as opposed to crack initiation) due to delayed hydride cracking. DHC propagation is variously referred to in this paper as DHC, DHC velocity, or DHC rate. Emphasis is mainly on DHC in cold worked Zr–2.5Nb pressure tube alloys used in CANDU™[1] and other Pressurized Heavy Water Reactors (PHWR). In this material, hydrides observed by optical metallography have a plate-like structure with the plates lying on the axial–transverse plane of the pressure tube. These hydrides are referred to as transverse or unreoriented hydrides. DHC in these pressure tubes occurs along the axial–radial plane and is the result of hydrides that have precipitated and grown on this plane. These hydrides are referred to as radial or reoriented hydrides. The hydrides observed using optical metallography are actually a collection of smaller hydrides (reference given further on), when observed at higher magnification. In the theoretical description of hydrides observable at size scales of the order of μm, these hydride clusters are idealized as consisting of a fully dense hydrided region that approximates the shape of the outlines of these clusters and are referred to simply as hydrides.

For simplicity in dealing with the essential thermodynamic description of the effect of dissolved hydrogen in a hydride-forming metal, the alloy is regarded as being a binary metal–H system. For the temperature range of interest from ambient to somewhat above 300 °C, the low or dilute hydrogen-containing region is the alpha zirconium phase. This phase is also referred to as the matrix. The concentration when the hydrogen in the alpha phase reaches its terminal solubility at which the hydride phase forms in equilibrium with the alpha phase is generally referred to in the literature on zirconium and its alloys as the Terminal Solid Solubility (TSS), but will in this paper generally be referred to as the solvus, as it seems to better describe its representation in standard temperature–composition binary phase diagram plots. The external work done on or by the Zr–H system in introducing or removing a hydrogen atom in either the alpha or hydride phase under stress is referred to as the hydrogen interaction energy. Similarly, when a portion of the alpha phase is converted to the hydride phase under stress, the external work done is referred to as the hydride interaction energy. The internal energy generated in the hydride and the matrix upon phase conversion from the alpha to the hydride phase is referred to as the coherency strain energy (or strain energy) when it is produced as elastic strain energy and as plastic work when part of the transformation strain produces plastic deformation. If the energy

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[1] CANDU is a trademark of Atomic Energy of Canada Limited, Mississauga, Ontario, Canada.

generated due to this conversion consists of both coherency strain energy and plastic work contributions it is called the hydride–matrix accommodation energy or simply accommodation energy. The transformation strains of the hydride phase are a measure of the shape and volume changes produced when converting a volume of alpha phase to the hydride phase with both phases assumed to be in their single-phase, unconstrained state. These transformation strains have in the literature also been referred to as the stress-free strains or eigenstrains of the phase transformation. (It should be noted that there are different ways that these transformation strains can be determined, both experimentally and theoretically, resulting in different results for their magnitudes, which then result in differences in quantitative predictions of DHC made with theoretical models.) The strains existing at the hydride–matrix interface when the hydride phase is embedded in the alpha phase and when there has been elastic and plastic accommodation between the two phases are called the constrained strains.

3. Physical features of DHC

The earliest experimental observations of DHC suggested that it is a diffusion driven process consisting of the repeated precipitation and growth of reoriented (radial) hydrides at a flaw under tensile stress to some critical size that causes the hydrided region to fracture along its length [13]. The fracture of the hydride at the crack causes an abrupt increase in length of the flaw which is generally up to the radial hydride's length along the crack plane, after which the foregoing process repeats itself. Direct confirmation of this step-wise sequence of events characterizing DHC was obtained in a limited number of TEM experiments in different hydride-forming metals [14–17], while indirect confirmation was obtained from metallographic and fractographic observations of hydrides at the crack tip and striation spacings, respectively [18]. In some favourable cases these observations could be correlated with corresponding step-wise intervals of acoustic emission and electrical resistivity signals [19–21] corroborating the metallographic and fractographic evidence of step-wise growth and fracture of the hydrided region. The key observation, relevant to the subsequent discussion of Kim's model, which could be inferred from these observations, is that, during each crack propagation step, the first requirement for DHC is that a new, radially-oriented hydride must be able to form at the flaw after each propagation step. (This implicitly means that at the start of each new propagation step the concentration of hydrogen at the flaw must first be able to increase to a concentration in the alpha phase sufficient for it to result in nucleation of a new radial hydride at the flaw.)

4. Original model of DHC

The first published version of the old DHC model was presented in 1975 September at a conference on the "Effect of Hydrogen on Behavior of Materials" [7]. The derivation of this version was subsequently reproduced in [13], but omitting the initial steps given in [7] in which the requisite expressions for the chemical potentials are derived. An analytical expression for DHC was produced and the predictions derived from this result compared with the extant experimental results of DHC velocity in specimens cut from unirradiated, cw Zr–2.5Nb pressure tubes. It should be noted that in [7,13] the sign convention used for stress was that tensile stress has a negative sign (favoured by geologists), which is opposite to the usual convention in the metallurgical literature of choosing a positive value for tensile stress. All subsequent refinements of the model used this latter sign convention.

The basis of the old DHC model is that the chemical potential for hydrogen in either the alpha-Zr or the hydride phase is determined by the entropy of mixing, which determines its hydrogen concentration dependence, and by the interaction energy, which, to be consistent with the convention used in mechanics, is assumed to be negative when this interaction results in a reduction in the energy of the system (the body of the solid and its loading system for an externally stressed solid). This would be the case when the sign convention for tensile stress is positive; so this initial version of the old DHC model did not adhere to this sign convention for interaction energy which was employed in later versions of the model. For simplicity it was assumed that the transformation strain produced by hydrogen when it is introduced into both the alpha and hydride phases is isotropic. This transformation strain is then fully characterized by the hydrogen molar volume of solution in zirconium or hydride, which is the change in the volume of pure zirconium or hydride when a mole of hydrogen is introduced. The interaction energy in this simple case is given by the product of the hydrostatic stress, p, and the molar volumes, $\overline{V}_H$, or $\overline{V}_H^h$ of hydrogen when it is introduced into the alpha or the hydride phases, respectively, under stress. The interaction energy then is $-p\cdot\overline{V}_H$ or $-p\cdot\overline{V}_H^h$, respectively, when the sign convention for tensile stress used in later versions of the model is employed. In the following reprise of the formulation of the initial version of the old DHC model, we will use this sign convention, which is consistent with its use by others in the metallurgical literature and in subsequent versions of the model.

The chemical potential μ_H^D driving diffusion of hydrogen in the alpha phase in a solid under an arbitrary hydrostatic stress, $p(r)$, that varies with position, r, is given by

$$\mu_H^D(r,p) = \mu_H^o + RT\ell n c_H^D(r,p) - p(r)\cdot\overline{V}_H \tag{1}$$

where μ_H^o is the chemical potential for an arbitrary reference level, $c_H^D(r,p)$ is the concentration of the diffusible hydrogen, which can vary with position and stress, and R and T have their usual meaning. It will be seen in the following that μ_H^o does not need to be specified for the cases considered. The variation of $c_H^D(r,p)$ with stress is obtained by noting that at zero stress, from Eq. (1), we have

$$\mu_H^D(r,0) = \mu_H^o + RT\ell n c_H^D(r,0) \tag{2}$$

Equilibrium between the regions at zero stress and at arbitrary stress is obtained when the chemical potentials for diffusion given by Eqs. (1) and (2) are equal. This yields that, at equilibrium, the concentration in the stressed part of the crystal is increased over that in the unstressed part according to

$$c_H^D(r,p) = c_H^D(r,0)\cdot exp\left[p(r)\cdot\overline{V}_H/RT\right] \tag{3}$$

When hydrides are present in the unstressed region, we obtain from Eq. (3):

$$c_H^{D,o}(r,p) = c_H^s(r,0)\cdot exp\left[p(r)\cdot\overline{V}_H/RT\right] \tag{4}$$

In which $c_H^s(r,0)$ is the solvus concentration for hydride phase equilibrium under zero external stress at location, r. This concentration will be used as the reference concentration when solving for the boundary concentrations at hydrides at the crack tip and in the bulk derived further on and, therefore is identified with the superscript 'o' to identify it as such.

Reference is usually made to [22] for the formulation of the effect of stress on chemical potential for a mobile interstitial element such as hydrogen or carbon in a metal lattice, although there may be earlier publications where these relationships were demonstrated.

When the hydrogen concentration in the alpha phase has reached its terminal concentration (solvus concentration) in a uniformly stressed solid, or locally at a hydride under stress, $p(r)$, the chemical potential of hydrogen at the hydride is given by (ignoring local variations of hydrogen concentration around a hydride due to stress variations arising from the Gibbs–Thomson and the coherency strain effects, which would average out when comparing equilibrium concentrations between hydrides of similar sizes at different locations):

$$\mu_H^B(r,p) = \mu_H^o + RT\ell n c_H^B(r,p) - p(r)\cdot \overline{V}_H + p(r)\cdot \overline{V}_H^h \tag{5}$$

The chemical potential in Eq. (5) is identified by the superscript '*B*' to indicate that this is the boundary chemical potential of hydrogen in local equilibrium with hydrides at location, *r*. That is, it is the chemical potential of hydrogen in solution in the alpha phase for the solvus at location, *r* and, therefore, determines the boundary concentrations at different *r* locations for the solution to the diffusion equation.

In this simple representation of the hydride interaction energy, no account is taken of any anisotropy in the volume changes which result from the crystal structure differences between the alpha and the hydride phases and/or differences in the symmetry of the interstitial sites in the alpha and hydride crystal lattices in which the hydrogen atoms are located. Later treatments take account of these crystal structure changes in the interaction energy by employing the hydride's transformation strains rather than the molar volume of hydrogen in the hydride phase in the interaction energy expression. In this initial model, the reference solvus concentration $c_H^s(r,0)$ from which the effect of external stress on the solvus is determined was taken to be that for phase equilibrium in an incoherent solid since the changes of the solvus concentration due to coherency strains and plastic work contributions, the latter resulting in hysteresis, had not been appreciated at the time of formulation of the model and it was assumed that the solvus data available at the time represented a fully reversible and unique temperature–composition phase relationship.

The hydrogen concentrations in equilibrium with crack tip and bulk hydrides at $r = \ell$ and *L*, respectively, which are the solvus concentrations as affected by external stress, are obtained by the condition that the chemical potential for diffusion must be equal to the boundary, or local solvus chemical potentials. For $r = \ell$, equating $\mu_H^D(r,p)$ given by Eq. (1), with $\mu_H^B(r,p)$ given by Eq. (5) and choosing as the reference concentration for $c_H^D(r,p)$ the value given by Eq. (4), yields:

$$\begin{aligned}&\mu_H^o + RT\ell n c_H^B(r,p) - p(r)\cdot \overline{V}_H + p(r)\cdot \overline{V}_H^h\\ &\quad = \mu_H^o + RT\ell n c_H^{D,o}(r,p) - p(r)\cdot \overline{V}_H\end{aligned} \tag{6}$$

This yields, after some algebra, the following boundary (solvus) concentration at $r = \ell$:

$$c_H^B(\ell,p) \equiv c_H^s(\ell,p) = c_H^s(0)\cdot exp\left[p(\ell)\cdot(\overline{V}_H - \overline{V}_H^h)/RT\right] \tag{7}$$

A similar derivation applies for the boundary condition at $r = L$ giving

$$c_H^B(L,p) \equiv c_H^s(L,p) = c_H^s(0)\cdot exp\left[p(L)\cdot(\overline{V}_H - \overline{V}_H^h)/RT\right] \tag{8}$$

We can express Eqs. (7) and (8) in terms of the reference concentration, $c_H^{D,o}(r,p)$, given by Eq. (4), yielding:

$$c_H^B(\ell,p) \equiv c_H^s(\ell,p) = c_H^{D,o}(\ell,p)\cdot exp\left[-p(\ell)\cdot \overline{V}_H^h)/RT\right] \tag{9}$$

$$c_H^B(L,p) \equiv c_H^s(L,p) = c_H^{D,o}(L,p)\cdot exp\left[-p(L)\cdot \overline{V}_H^h)/RT\right] \tag{10}$$

This remarkable result shows that, with reference to the concentration gradient imposed by the stress gradient, the boundary concentrations driving diffusion between crack tip and bulk hydrides now show a strong effect of stress. This result for the boundary concentrations anticipates the net concentration difference between bulk and crack tip hydrides governing the steady state hydrogen diffusion rate given by Eqs. (15)–(17) further on.

In reviewing the three publications in which the relationship for the effect of external stress on the solvus [7,9,11] is derived, the first of which is reproduced in the foregoing, the author noted that the derivation in [11], which is based on use of the Moutier cycle, is not correct in some of the steps, although the final result is correct, because the errors made in some of the Moutier cycle steps in [11] cancel each other. In Appendix A the corrected version of this derivation is given.

There are a number of important points concerning the foregoing derivation, all which concern the sign of the interaction energies. When determining the direction of diffusion of hydrogen due to stress and concentration differences between two locations it is important that each location is treated consistently with the other. As mentioned, the sign of the interaction energy in the expression for the chemical potential for diffusion given by Eq. (1) is chosen to be consistent with the usual sign convention employed in mechanics while also ensuring that when the hydrogen concentration is increased the entropy of mixing is increased. The chemical potential for the boundary condition at hydrides at a particular location, *r*, given by Eq. (5) must then be consistent with this choice of sign convention for the chemical potential for diffusion. This choice of sign convention results in a positive interaction energy for the volume of hydrogen placed from the alpha into the hydride phase and a corresponding negative one for the hydrogen volume added to the hydride phase, while the opposite signs would prevail if the process were reversed. Although it transpires that the consequent stress-driven diffusion flux results in the transfer of hydrogen between matrix and hydride in the bulk, at $r = L$, being opposite to that at the crack tip at $r = \ell$ the boundary chemical potentials at each location must be treated on the basis of a common reference state in order for the boundary and diffusion chemical potential values to be physically consistent with each other.

Eq. (7) shows that if the volumes of formation for hydrogen are the same in the matrix and in the hydride phases, then there would be no change in the solvus of hydrogen in the alpha phase under a uniform external stress compared to one without such a stress. This means that the terminal solubility of hydrogen in zirconium would be unaffected by external stress in a closed system (no external source of hydrogen present) if there is no net volume change per atom or mole of hydrogen when converting a quantity of matrix phase containing hydrogen in solution to hydride phase or vice versa. In [7,13], because the data at the time gave a value for $\overline{V}_H$ that was approximately half that for $\overline{V}_H^h$, it was concluded that there was also an effect of stress on the solvus concentration in addition to the effect of stress on hydrogen in solution. As a result, it was thought at that time that the most important effect of stress on the diffusion flux was the concentration difference between the bulk and the crack tip hydrides with the flux due to the stress gradient playing a secondary role and statements to that effect were made in [13]. However, examination of the contribution of $\overline{V}_H$ to the effect of stress on the local solvi concentrations shows that, depending on its magnitude, ranging from it being equal to $\overline{V}_H^h$ to being equal to zero, its relative contribution to the diffusion flux of hydrogen to the crack tip hydrides via the stress gradient ranges from it being the sole contribution to the flux to not contributing to it at all, with the other component being the diffusion flux due to the concentration gradient. When $\overline{V}_H$ is assumed to be zero there is no effect of the stress gradient on the diffusion flux, but the effect of external stress on the solvus has its correspondingly maximum possible value. Because the contribution of $\overline{V}_H$ to the interaction energy for hydrogen in the matrix is contained in both the chemical potential for diffusion (and hence in the mathematical formulation of the diffusion equation) and in the boundary solvus concentrations, the relative contributions of the two volumes (and the diffusion fluxes that result from them) are automatically accounted for in the solution to the diffusion equation. The correct result is obtained regardless of the numerical values of the respective molar volumes of hydrogen in the hydride and matrix phases and the corresponding sources of diffusion (stress or concentration gradient) driving hydrogen to the crack tip hydrides. In Kim's model (see, for instance [4]), he assumes that only the hydride interaction energy term is affecting the solvus under external stress, thus getting the maximum possible effect of external stress due to differences in local solvi values between high and low stress regions while also assuming that the diffusion flux contains only diffusional contributions from the resulting difference in solvi between the crack tip and bulk regions. This formulation is certainly internally consistent, but is entirely ad hoc and does not reflect the experimental observation that, in fact, $\overline{V}_H \approx \overline{V}_H$, nor does it reflect the universally accepted fact in the international literature that a tensile stress gradient drives positively misfitting, mobile interstitials such as hydrogen to regions of highest stress. Kim gets the correct (linearized) one dimensional diffusion flux expression in this artificial case because the errors in his treatment exactly cancel, but the formulation is based on faulty physical reasoning and would give numerically correct results for the flux only in the special case considered, and which, of course, is also inconsistent with the experimental values for the hydrogen formation volumes.

Examining the expressions for the chemical potentials for diffusion, Eq. (1), and for local equilibrium with hydrides, Eq. (5), we can use these equations to demonstrate how the effect of stress redistributes hydrogen in solution and causes hydrides to grow preferentially in the region under stress at the expense of the hydrides under no, or lower, stress.

Consider that we have two specimens containing hydrogen, one under a uniform external tensile stress, the other under no external stress, both of which are closed to external transfer of hydrogen. We initially assume that both specimens each have a total hydrogen content given by c_H^o which is less than that of the solvus concentration. If we now bring these two specimens together and allow interchange of hydrogen atoms between the two specimens and also assume that the specimen under zero stress is much larger than that under stress so that there is negligible depletion of hydrogen in the specimen under no stress, then hydrogen will diffuse from the specimen under no stress to the one under stress because the chemical potential is initially lower there by $-p \cdot \overline{V}_H$ and their starting hydrogen concentrations are the same. At equilibrium the chemical potentials of the two specimens must be equal. This means that the concentration in the specimen under stress will increase to a concentration, c_H^D, given by Eq. (3) with $c_H^D(0)$ replaced by $c_H^o(0)$ (dropping the r-dependence). If the hydrogen concentration in the specimen under stress reaches the concentration of the solvus, then hydride will form in the specimen under stress, even though the concentration in the specimen under no stress is insufficient for this to occur there. The hydride will continue to grow in the specimen under stress until the entire specimen becomes solid hydride, provided there is no depletion of the hydrogen in the specimen under no stress.

Now consider the case where the total initial hydrogen content in the specimen under no stress exceeds that of the solvus. Then the hydrogen concentration in this specimen, denoted by $c_H^D(0)$ in Eq. (3) would have its maximum possible value, which is the solvus concentration, denoted by $c_H^s(0)$. This yields the stress dependence given by Eq. (4).

Now, if the increase in concentration that would occur when equilibrium is achieved between the two specimens is sufficient to reach c_H^s in the stressed specimen, then hydride would form there and the hydrogen concentration would not be able to increase further. Hence the chemical potential for hydrogen in solution in the stressed specimen would never be able to reach its value that would result in equality of the chemical potential of hydrogen in solution between the stressed and unstressed specimens. This means that equilibrium between the two coupled specimens, one of which is under stress, the other of which is not, is impossible when hydrides can exist in both specimens. Since equilibrium is impossible, once hydrides are able to precipitate, they would continue to grow in the stressed specimen at the expense of the hydrogen/hydride in the unstressed specimen as long as the stress difference is maintained and there is sufficient hydrogen (hydrides) in the specimen under zero stress. Note that in this model, in which it is assumed that the dissolution and precipitation solvi have the same value at a given temperature, any stress greater than zero would result in hydride growth in the stressed specimen if the total starting hydrogen content in both specimens were initially at or above that for hydride formation. (However, a threshold stress would have to be exceeded for reoriented (radial) hydrides to precipitate (nucleate and grow) in the stressed specimen.)

In formulating the old DHC model, the assumption was made that the concentration of hydrogen in the specimen is such that when a stress is applied to a specimen with a flaw, the stress increase in the flaw causes a sufficiently large increase in hydrogen concentration there for hydride nucleation to be possible. That is, hydrides are assumed to pre-exist at the flaw as well as in the bulk. Whether this assumption is correct or not can be calculated on the basis of the equilibrium conditions given by Eqs. (3) or (4) assuming that the difference between the hydrogen concentration for the solvus for hydride precipitation is not much different from the concentration required for nucleation, the latter requiring that there is sufficient chemical driving force above the precipitation (nucleation) solvus for the hydride surface energy barrier to be overcome. It was further assumed that the time required for this concentration increase at the flaw tip, which is needed to nucleate a hydride at the start of each DHC propagation step, is negligible compared to the time for the nucleated hydride to increase in size to its critical size for fracture. This greatly simplifies the solution of the diffusion solution as steady state conditions would then apply since the dissolving hydrides in the bulk and the growing hydrides at the flaw would fix the concentrations at their respective local solvi values.

At the time of the formulation of the first version of the old model, the significance of the difference in terminal solubility of hydrogen for hydrides when dissolving (generally detected in heating experiments) and when precipitating (generally detected in cooling experiments) and the constraint on the directionality of the flow of hydrogen between matrix and hydride, had not been appreciated. Therefore, in the first version of the old DHC model, the solvus for dissolving hydrides was assumed to be the same as that for precipitating ones. A consequence of this assumption is that, provided that the total hydrogen content is such that hydrides can be present everywhere in the solid, hydride growth is always possible at a flaw in a specimen under external stress provided there is a finite stress difference between the flaw tip hydrides and the hydrides in the bulk of the specimen. (Of course, as stated in the foregoing, with decreasing stress difference it would become increasingly more difficult to precipitate and grow radial hydrides (i.e., for the stress to be sufficient to reorient hydrides at the crack tip).) A further consequence of the assumption of no hysteresis in the solvus is that DHC is possible regardless of direction of approach to the test temperature.

Now with the diffusion potential given by Eq. (1) and referring to Fig. 1, which has been reproduced from [7,13], we wish to calculate the flux of hydrogen, J_H, (per unit depth of crack) into the cylinder centred at $r = \ell$. The diffusion equation is:

$$J_H = -\frac{c_H^* \cdot D_H}{RT} \nabla \mu_H^D \equiv -\frac{c_H \cdot D_H}{\Omega_{Zr} \cdot RT} \nabla \mu_H^D \qquad (11)$$

In Eq. (11): c_H^* is number of hydrogen atoms/unit volume, c_H the atom fraction of hydrogen in α-Zr, D_H the diffusion coefficient of hydrogen in α-Zr, Ω_{Zr} the atomic volume of Zr in α-Zr and μ_H^D defined by Eq. (1)

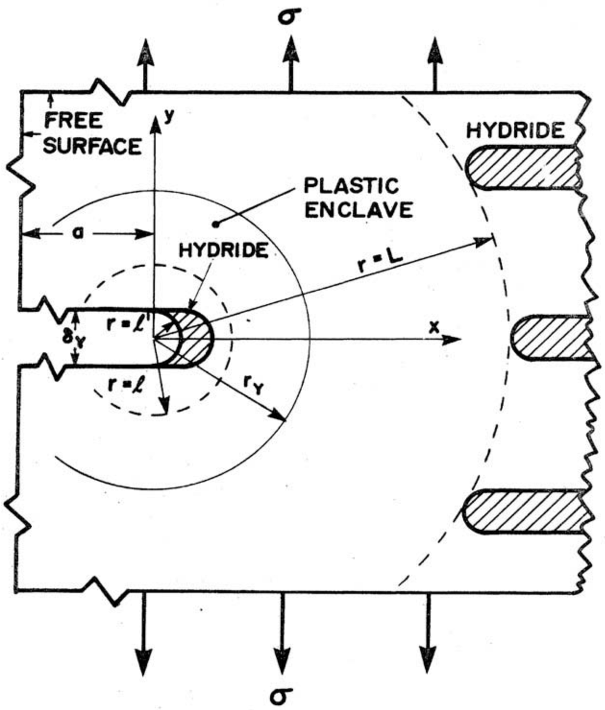

Fig. 1. Crack and diffusion geometry (from [7]).

To solve Eq. (11), the following assumptions were made: (a) growth occurs under steady state conditions, (b) any hydrogen entering into the crack tip region at $r = \ell$ is converted into hydride lying on the crack plane with shapes corresponding to those observed experimentally and (c) the nearest hydrides away from the crack tip are at $r = L$, where L is the average inter-hydride spacing. Fig. 1 has been reproduced from the original references to clarify a number of points that were omitted in these references concerning these assumptions and the figure. The first is that it was implicit in the original formulation that DHC crack propagation could be either in the axial or radial direction of pressure tubes of CANDU reactors or PHWRs, which means that the crack plane is the radial–axial plane. As mentioned in Section 3, in these tubes, the pre-existing (bulk) hydride platelets are transverse or circumferential hydrides that have their platelet normals predominantly oriented in the tube's radial direction. When hydrides can nucleate and grow at the crack tip, they are reoriented as axial–radial hydrides on this plane (because, when the crack tip stresses are sufficient to nucleate and grow hydrides they are also sufficient to reorient the newly formed hydrides to fall on the radial–axial plane). These radial hydrides (they could also be designated as axial hydrides depending on the dominant crack growth direction) have their plate normals in the transverse direction. Both sets of hydrides, despite them being differently oriented, are assumed to lie on the near-basal planes of the hcp lattice of the Zr alpha phase since this habit plane results in them having the lowest strain or accommodation energies. Therefore, they would have the same solvus in the externally unstressed state. For the crack propagation plane considered, forming hydrides on their preferred habit plane is possible in pressure tubes because both sets of planes contain a sufficiently large fraction of resolved basal poles in these two plane normal directions for a fairly dense cluster of hydrides with similar orientation to be possible. In Fig. 1 the bulk hydrides at L are shown to have the same orientation as the axially–radially oriented crack tip hydride. This is done for simplicity of representation; the actual, transverse, hydrides would either have their plate normals in the x-direction or out of the plane of the paper (in the implicit z-direction), depending on whether the crack growth direction depicted is the radial or axial one, respectively.

Condition (a) in the preceding paragraph is satisfied when

$$\nabla \cdot J_H = 0 \tag{12}$$

Combining Eqs. (1) and (11) with (12) yields the following differential equation (note that there are misprints in Eqs. (10) and (12) of [7]):

$$\frac{1}{r}\frac{d}{dr}\left[r\frac{dc_H}{dr} - r\frac{c_H}{RT}\overline{V}_H\frac{dp}{dr}\right] = 0 \tag{13}$$

This equation is solved for the steady state diffusion flux, J_H(*steady state*) subject to the boundary conditions given by Eqs. (9) and (10). This yields:

$$J_H(steady\ state) = -\frac{D_H c_H^s}{r\Phi\Omega_{Zr}}[E_L - E_\ell];$$

$$\Phi = \int_\ell^L dr^{-1} exp\left[-p(r)\cdot\overline{V}_H/RT\right] \tag{14}$$

where E_L and E_ℓ are defined in Eqs. (16) and (17) in the following. Following the derivation in [7,13] for the conversion of the diffusion flux to the hydride growth/fracture rate yields the following proportionality for the DHC velocity, V_{DHC}:

$$V_{DHC} \propto [E_L - E_\ell] \tag{15}$$

with

$$E_L = c_H^s exp\{-p(L)\overline{V}_H^h/RT\} \tag{16}$$

and

$$E_\ell = c_H^s exp\{-p(\ell)\overline{V}_H^h/RT\} \tag{17}$$

As stated in the foregoing, this remarkable result makes it appear as though the diffusion rate is determined by a concentration difference between bulk and crack tip hydrides suggesting that the solvi at these two locations are significantly affected by stress even though, locally, as seen by Eqs. (7) and (8), or equivalently in a closed system under uniform stress, they would not be if there were no net volume change in transferring a hydrogen atom from the matrix to the hydride phase. This is exactly the driving force for DHC that Kim, as is discussed in Section 7, claims is a new feature in his DHC model. Further discussion of this point is given in Section 7 where Kim's new DHC model is discussed. A general explanation of this apparent effect of stress on what appear to be crack tip and bulk solvi concentrations as given by Eqs. (15)–(17) was subsequently provided by Flanagan and co-workers [23]. Their explanation for this strong effect of stress on the concentration difference governing the steady state diffusion flux supports the result given in this paper.

In the final version of the old model [10], where use is made of the experimentally determined solvi for hydride dissolution and precipitation and the hydride's transformation strains are used for the determination of its interaction energy, as discussed further on, the following relations apply for E_L and E_ℓ:

$$E_L = c_H^{heat} exp\{\overline{w}_t^a(L)/RT\} \tag{18}$$

$$E_\ell = c_H^{cool} exp\{\overline{w}_t^a(\ell)/RT\} \tag{19}$$

using the notation of [10], where c_H^{heat} and c_H^{cool} are the experimentally determined solvi for hydride dissolution and precipitation under zero applied stress, respectively, and $\bar{w}_t^a(L)$ and $\bar{w}_t^a(\ell)$ are the hydride interaction energies at the dissolving and precipitating hydrides at L and ℓ, respectively, with

$$\bar{w}_t^a = -\frac{\overline{V}_{Zr}}{x}\cdot\sigma_{ij}\cdot e_{ij}^T \tag{20}$$

and $\overline{V}_{Zr}$ is the partial molar volume of zirconium, σ_{ij} the applied stresses, e_{ij}^{T} the stress-free transformation strains to transform Zr to zirconium hydride and x the composition of hydride phase (ZrH_x).

In most of the papers published by this author including [10], the molar volume of the interaction energy used in Eq. (20) was $\overline{V}_{hydride}$. This is incorrect as the volume change on transforming the matrix to hydride that is given by the transformation strains is measured from the volume of the matrix phase, which is given by $\overline{V}_{Zr}$. The factor, x, accounts for the number of hydrogen atoms that need to be transferred between the two phases per Zr atom of the matrix phase. This factor was either explicitly included in Eq. (20) when $\overline{V}_{hydride}$ is calculated per mole hydride or factored into $\overline{V}_{hydride}$ when calculated per mole H. In the paper by Simpson and Puls [8] it was inadvertently omitted, since the former value of $\overline{V}_{hydride}$ was used in numerical evaluations and, therefore, this factor needed to be explicitly included. For the same reason, the factor, x, should also have appeared in the denominator of the expression in the exponential involving $\bar{w}_{t}^{inc}$, which is the hydride–matrix strain energy in forming the hydride. That paper also should have had the signs reversed in front of the expression in Eq. (1) of [8] giving the total arrival rate of hydrogen atoms and in the arguments for the exponentials. This error presumably arose because, in copying this result from [7,13], the sign convention in [8] for tensile stress had been changed to the conventional one employed in the metallurgical literature. In [8], it was also stated regarding Eq. (1) in [8] that "*the principal driving force giving rise to Eq. (1) is the difference in local hydrogen concentration between hydride platelets close to and remote from the crack tip*" which is misleading as it implies that these concentrations are solvi concentrations affected strongly by stress, which, as explained in the foregoing, is not true.

After the development of the first version of the DHC model, a realization emerged, both from experimental and theoretical studies, that there is a reproducible difference in the solvus for hydride dissolution compared to that for hydride precipitation with the solvus for hydride precipitation being higher than that for dissolution at a given temperature. In the literature on Zr–H systems these solvi are generally referred to, respectively, as TSSD and TSSP (Terminal Solid Solubility for Dissolution and Terminal Solid Solubility for Precipitation). They are given these designations because, in most cases, they are experimentally detected only at their terminal points (i.e., the last quantity of hydride to dissolve or the first to precipitate/nucleate). It has been implicitly assumed that these terminal concentrations define the solvi concentrations no matter what would be the volume fraction of hydrides. This is likely not true due to the coherency strains produced by the hydrides [24–29]. A study is needed to determine how these coherency strains affect the solvus concentration as a function of the hydride volume fraction. Despite the hysteresis, these solvi boundaries are reproducible under repeated measurements and for different specimens when using the same detection technique and under similar experimental conditions. Based on our current understanding, the salient points for DHC of these properties of the solvi for dissolution and precipitation are as follows.

At a given temperature, the solvus for hydride dissolution defines the terminal hydrogen concentration in the alpha phase only for a process of hydride dissolution; conversely the solvus for precipitation (either of new hydrides or on or near pre-existing hydrides) defines the terminal hydrogen concentration in the alpha phase only for hydride precipitation. In the same material, the solvus for precipitation depends, however, much more strongly on the experimental conditions and prior thermo-mechanical history of the material than does the solvus for dissolution, there being a range of solvus concentrations for precipitation, the upper and lower bounds of which (in terms of concentration at the same temperature) have been designated by Pan and co-workers [30], respectively, as TSSP1 and TSSP2. The reason for the wide range of values for the solvus for precipitation has been speculated by Puls [30] to be due to the difference in energy required to nucleate or to grow pre-existing hydrides, respectively, but there is no direct experimental confirmation of the correctness of this speculation. A theoretical explanation for the hysteresis between precipitating and dissolving hydrides is based on the generation of irrecoverable work of plastic deformation due to the large hydride transformation strains when hydrides form or dissolve. The first quantitative attempt to recognize the contribution of this plastic work to the accommodation energy and make an estimate of it was by Paton and co-workers [31] followed by [32–34,11,12].

The first revisions to the solvi equilibrium conditions accounted for the coherency strain produced by the hydride transformation strain on the solvus, in addition to the effect of external stress on the solvus. Note, however, that it did not consider the possibility that some of the coherency strain could be reduced by plastic deformation, only that the fully coherent hydride could have different strain energy due, possibly, to its 'size'. Incorporation of this model for the solvus by Puls led to a revision of the old DHC model [8]. This version allowed for the possibility of there being a lower solvus concentration at the source hydrides in the bulk under low stress compared to at the sink hydrides growing at the crack tip under high stress, the difference in the solvus concentrations being attributed to a lower coherency strain energy contribution to the solvus for the hydrides in the bulk compared to those at the flaw. Due to the higher solvus concentration for the hydrides at the flaw in this model there would now need to be a sufficiently large stress magnitudes prevailing at the flaw to ensure that the increase in hydrogen concentration is sufficient for hydride precipitation to be possible there. Since the stress in the plastic zone at the flaw would decrease with increasing temperature (due to the dependence of the yield strength on temperature), there would then be a temperature for which the increase in hydrogen concentration at the flaw would be insufficient for hydride precipitation. It was further conjectured that the reason DHC was possible above this temperature when the test temperature was approached from above was because this resulted in the formation of bulk hydrides having strain energies that are of similar magnitude as those formed at the flaw, thus effectively eliminating the disparity in solvi concentrations between the hydrides at the two locations. Ambler [35] subsequently used this model of the TSS to determine what values of hydride–matrix strain energies would result in the experimentally determined arrest temperatures.

Based on the work of Eshelby [36,37], if coherency is maintained between hydride and matrix, there would not be a size effect on the strain energy (i.e., the strain energy is the same regardless of the total volume of the hydride). However, if the hydrides formed had different shapes or different transformation strains, then there could be differences in the strain energy depending on prior thermo-mechanical conditions of the specimens. An example of the case of different transformation strains is the difference in these between delta and gamma hydrides or the differences that could apply when the hydrides first nucleate and when they grow in size (see further on.) Hence, it is possible that there could be differences in strain energy contributions alone that could contribute to changes in the solvus concentrations and there might not be a need to invoke a work-loss mechanism if it could be shown experimentally that the foregoing were the cause of the differences in the solvi concentrations.

At a later stage, since the transformation strains of either the gamma or the delta hydrides are well above the elastic limit strain [12], it was thought that these strains would likely be relaxed by plastic deformation (except when hydrides are very small, such as at nucleation). The result would be a much lower, as well as a yield-strength-dependent hydride–matrix accommodation energy compared to the corresponding fully coherent elastic strain energy. The physical reason for the hysteresis in the TSS then arises from the unrecoverable plastic work produced in forming and dissolving a hydride. There can be no true (i.e., fully reversible) equilibrium among the hydrides when the material is maintained at a constant temperature because the hysteresis is the result of irrecoverable work in forming or dissolving the hydrides. The hydrides are either in a dissolving or in a forming state. They cannot adjust their volume fraction by a reversible exchange of hydrogen at constant temperature or stress. To change the direction of the phase transformation requires the input of external energy, either by changing the specimen's temperature or by adding or removing hydrogen from an external source. The consequence of this directionally limited 'equilibrium' of the hydrides is that it increases the importance of the stress-gradient-driven increase of hydrogen to the crack tip in overcoming the opposite concentration difference between the solvi concentrations of dissolving and precipitating hydrides. One way to eliminate this concentration difference is by cooling to the test temperature, which results in an initial hydrogen concentration value in solution everywhere in the sample – including at the crack tip – corresponding to that given by the solvus for precipitation. However, during DHC the bulk hydrides in this case would not be available as a source of hydrogen to replace those in the alpha phase which had diffused to the crack tip until the concentration in the bulk had been reduced to the solvus concentration for hydride dissolution at that temperature.

These experimentally observed and theoretically rationalized properties of the solvus can provide a physical explanation of the effect of direction of approach on DHC propagation [8,10,38,39] in terms of the old DHC model. Provided the specimen contains sufficient hydrogen for the bulk of the specimen to exceed, over the temperature range of testing, the solvus for hydride dissolution and that the temperature is not so high that hydride fracture is still possible under the stresses prevailing at the crack tip, then the reduction with increase in temperature of the maximum tensile stress at the flaw eventually results in there being insufficient increase in hydrogen concentration at the flaw for the solvus for hydride formation to be reached. Above this temperature, DHC would only be possible by increasing the hydrogen concentration in the bulk of the specimen. This can be done by approaching the test temperature from above, the maximum increase in bulk hydrogen concentration achievable being the difference in concentration between the solvus for hydride precipitation and the corresponding value for dissolution at the same temperature. As discussed in [10], in this case, the solution of the steady state model is not really applicable since the bulk hydrides – not being able to serve as sources of hydrogen in solution – do not ensure that a fixed hydrogen concentration is maintained in the bulk at a fixed location and therefore the rate of growth of the hydrided region at the flaw becomes time dependent as the hydrogen concentration gradient changes with time.

Predictions have been made of the temperature at which DHC would stop as the temperature is increased when approaching the test temperature from below using the old DHC model. Kim [5] claims that calculations made by Ambler [35] and Puls and co-workers [12,39] on the basis of the old DHC model have shown that the concentration of hydrogen at the flaw cannot reach the level of the solvus for precipitation when approaching the test temperature from below. In Section 5 we address Kim's assertion in detail by re-examining the analyses in each of the cited references. However, before proceeding with this discussion, we note that quantitative predictions of DHC arrest derived from such a simplified theoretical model is subject to large uncertainties, the most significant of which are discussed in the following.

In order to know whether the hydrogen concentration at the flaw would be sufficient to nucleate and then grow a hydrided region to its critical dimensions for fracture requires determining: (i) the magnitudes of the normal stress components at the flaw and any possible modifications to these stresses as hydrides are precipitated, (ii) the solvus concentration for hydride dissolution and (iii) the solvus concentration for hydride nucleation and growth. There are considerable uncertainties associated with all of these quantities.

Accurately calculating the stress elevation in the plastic zone of, say, cw Zr–2.5Nb pressure tube material is difficult, not the least because the material is elastically and plastically anisotropic. Moreover, there are currently no experimental methods available to verify that the calculated stresses are correct. The total hydrostatic stress at the flaw also depends on the value of the uniaxial yield strength. The value used is generally an average one from some data base, the bounds of which could range over ±75 MPa within two standard deviations of the mean. In addition, estimating the maximum stresses at the flaw prior to hydride formation may not be sufficient to obtain an accurate temperature of DHC arrest in all experimentally observed cases, since hydride nucleation may be possible, but growth of the hydrided region to a critical length may not be. Accurately determining the stress state and morphology of the hydrided region in or beyond the plastic zone as it forms requires knowledge of the transformation strains associated with the hydrided region as it grows (there are different possibilities for what these could be in the literature [40,41]) and a methodology for an elastic–plastic solid that can account for the effect of these transformation strains on the modification of the stress state of this region. Moreover, it is known from TEM and metallographic observations that the hydrided region, when examined at the highest practical magnification, does not actually consist of a fully dense hydrided region as it might appear under optical metallographic observations, but is composed of a dense cluster of much smaller hydrides [42,43]. The degree to which the coherency stresses in such a hydrided region have been relaxed by plastic deformation has not been firmly established and, therefore, large uncertainties are involved in estimating the stress state of a pre-critical hydrided region at a flaw.

Once the stresses at the flaw have been determined, the concentration obtained needs to be compared with the solvus concentration for hydride nucleation or growth. As shown, for instance, in [30], a large range of values is possible and one would have to speculate, as was done in [30] and [39], as to which value over the large range possible is applicable to the case of hydride nucleation and growth at the flaw.

Finally, the value of the solvus concentration for dissolution is required. This seems at first glance to be the least uncertain quantity in the calculation, particularly when compared to the large range of values obtained for the corresponding solvus for precipitation, but a closer examination reveals that there is also large scatter in these concentrations. In particular, almost all of the experimental measurements show increased scatter at temperatures below 200 °C, which is the temperature range of interest for DHC. In fact, there are only a few measurements of the solvus below a hydrogen concentration of about 7 wppm H. Moreover, the measurements at these low-hydrogen concentrations have a higher experimental uncertainty. Hence the solvus given below 180 °C relies mostly on extrapolation of fits to higher temperature data. This is, of course, also true for the solvus concentration for precipitation.

5. Review of previously published calculations of hydrogen concentration at a flaw and DHC arrest temperature

The earliest attempt to calculate the DHC arrest temperature when the test temperature was approached from below was that by Ambler [35]. Ambler was able to show on the basis of the old DHC model, which had been refined by Puls [9] using theoretical expressions for the solvi, that by a suitable choice of elastic strain energy values for the hydrides in the bulk, the model could account for the observed temperatures of DHC arrest when the test temperature was approached from below and could explain why DHC was possible when the test temperature was approached from above. He indicated that the explanation for the effect of direction of approach of test temperature provided by this analysis was essentially the same as that previously given by Simpson and Puls [8], although in that paper no attempt was made in calculating the arrest temperature.

In [12] Puls calculated the increase of hydrogen concentration in solution at the crack tip predicted by his model assuming an experimentally calculated value for the dissolution solvus in the bulk (denoted as being at position $r = L$ in the radial symmetry assumed for the steady state DHC model, Fig. 1) and a theoretically calculated value at the crack tip at the maximum stress position (denoted by $r = \ell$). This concentration is compared with the theoretically calculated solvus concentration for hydride precipitation prevailing at the crack. The calculation was done for illustrative purposes to get some idea of the magnitudes of the quantities involved given the uncertainties in the experimental data and the simplifications of the model and was done at only one temperature of 373 K. This calculation shows that at 373 K the solvus concentration would not be exceeded. (The value of $\overline{V}_H$ used in that calculation is lower by about a factor of two compared to the currently accepted value, but this has no effect on the calculated results because the contribution due to this volume cancels when comparing the ratio of the increase in the hydrogen concentration at the crack with the solvus concentration at the crack tip.) Although the difference becomes less with decreasing temperature, this calculation predicts that the same result would be true at ambient temperature. However, using the experimentally determined value for the solvus for dissolution, while assuming that the solvus for precipitation is shifted with respect to that solvus by $\exp\{\bar{w}_t^{inc}(\ell)/RT\}$ is inconsistent with the theoretical formulation of the effect of accommodation energy on the two solvi concentrations. This inconsistency forces the increase required at the crack tip in the hydrogen concentration by stress-assisted diffusion to be much larger than it would actually need to be for DHC to be possible. Rather, the reference solvus for both bulk and crack tip hydrides, which is the incoherent (stress-free) solvus concentration, c_H^s, should have been used. Later studies show that a value of 1000 J/mol, appropriate to the value of yield strength prevailing at 373 K, would not be an unreasonable value for $\bar{w}_t^{inc}(L)$ in relation to the choice of 4912 J/mol H for $w_t^{inc}(\ell)$ [44]. This modification to the analysis in [12] increases the predicted value for the solvus concentration for dissolution and the solvus concentration for precipitation would now be exceeded and DHC would be predicted to occur at 373 K when the temperature is approached from below. As stated in Section 4, there are many uncertainties in the data required for this calculation and this exercise simply demonstrated, in retrospect, the sensitivity of the predictions to the choice of data used within the range of their uncertainties. It does not suffice as proof that the model's thermodynamic basis is invalid.

Kim [4] cites the paper by Shi and co-workers [39] as failing to show that DHC is possible when the test temperature is approached from below. The analysis by Shi and co-workers incorporated the experimentally observed effect of hysteresis on the hydrogen solvus and calculated the critical hydrogen concentration and various critical temperatures at which DHC would no longer be possible. It is a simplified treatment that assumes, unlike the foregoing treatment by Puls [12], that any effect of external stress on the solvi concentrations is sufficiently small that it can be ignored. The analysis, therefore, makes use of experimentally determined solvi concentrations, which do not include any potential effects of external stress on the solvi. This is an approach that is also applied by Kim in his schematic illustration, using data from experimental solvi, in estimating the concentration difference driving hydrogen arrival rate at the crack tip based on his new DHC rate model. In Kim's model, though, this use of experimental, externally unstressed, solvi data is inconsistent with the assumption in his model that there is a large effect of external stress on hydride nucleation and, hence, on the hydride nucleation solvus. (In Appendix B, an estimate is made of the possible magnitude of the effect of external stress on the solvus based on two bounding choices for the hydride transformation strains. It is seen that for the two bounding cases of pure lattice strain and invariant plane strain there is an experimentally undetectable effect of external stress on the solvus.)

Although Kim concludes in [4] that the stated arrest temperature prediction for DHC is not met in [39], Fig. 7 in [39] clearly shows that DHC is possible up to ~150 °C when approaching the test temperature from below. The main reason for the better agreement with experiment compared to the result obtained by Puls in [12] is the higher total stress elevation at the flaw obtained at lower temperature because of the increase in Poisson's ratio with decrease in temperature. Also, theoretical estimates of highly uncertain quantities such as the hydride–matrix accommodation energy were avoided in this analysis with recourse taken, instead, to experimental values of the solvi concentrations. It is pointed out in [39] that "*by using a slightly higher yield stress than the value used by Ambler the T_A value observed by Ambler can be predicted very well*". This analysis further supports the point made in the preceding that estimates of the maximum hydrostatic stress at the flaw are highly uncertain.

6. Addressing Kim's assertion of the limitations of the old DHC model

The earliest publication in an international journal of Kim's rationale and ideas for a new DHC model appeared in [1]. Kim stated three perceived shortcomings in the predictions of the old DHC model. These are that the model cannot explain, (i) why the DHC velocity becomes constant regardless of the applied stress intensity factor, (ii) why DHC has a strong dependence on direction of approach to test temperature and (iii) why there is an effect of hydride size on DHC velocity. Kim then provided an alternative physical description to explain these effects, which he called Kim's new DHC model, although no actual mathematical formulation or analytical or numerical derivation of his new model was given; rather, the model's predictions relied on graphical arguments in terms of experimental data of Zr–H solvus temperature–composition boundaries measured on externally unstressed specimens.

In the following we present arguments, drawing on those made in Section 4 reprising the theoretical derivation of [7], showing that Kim's reasons for the shortcomings of the old DHC model are, in fact, incorrect. This is followed by an evaluation of the physical validity of the mechanism for DHC proposed by Kim as given specifically in [4] and in other publications [1–3,5,6].

Regarding Kim's first point, that the old model cannot explain why the DHC velocity becomes independent of K_I above its K_{IH} threshold, the author is presumably referring to the results given in [7,13] showing that the model predicts a small reduction in DHC propagation with K_I while the data shows little change in DHC rate with K_I. The reason for the predicted result from the old DHC model arises mainly from the assumption made at that time that the thickness of the crack tip hydride increases with K_I^2. A further reason for the K_I-dependence is that the distance chosen at which the hydrogen concentration in solution in the bulk is fixed was close enough to the crack tip that the stress field is still determined by K_I. The distance chosen (inter-hydride spacing) is somewhat arbitrary as points in the bulk that are further from this distance would also be able to contribute hydrogen in solution to the crack tip. These points were made in [10] and the predictions of the model with these restrictions removed show that the effect of K_I on DHC velocity has essentially been eliminated (see Fig. 2 in [10]). With the elimination of the K_I-dependence due to the foregoing contributions, it is now evident from the model why there is little K_I-dependence in the velocity since the stress difference between the crack tip and the bulk remains approximately the same with increase in K_I because the peak stresses in the plastic zone at the crack tip change little with applied K_I, only their location changes, and it is the former difference that is of greatest importance in determining whether or not one would have DHC propagation and what would be its rate. The effect of K_I on the location of the stress maximum at the crack tip, which would affect the shape of the stress gradient, is judged not to have an important effect on the DHC propagation rate. It should be noted that this explanation can also account for why a material with a higher yield strength value would have a higher DHC propagation rate, since the stresses in the plastic zone would increase with increasing yield strength, which would increase the stress-driven diffusion rate. This explanation of the effect of yield strength on the DHC velocity was, rejected by Kim in [3] on the basis that "*...this hypothesis is in contradiction to a constant DHCV* [V stands for velocity] *independent of the applied stress intensity factors or K_I's in excess of the threshold stress intensity factor*."

It should be noted that the approximations made in the model to obtain an analytic solution, which involves imposing boundary conditions such that steady state diffusion conditions apply, mean that the model is most applicable over a K_I-range for which the critical length of the hydrided region is less than the plastic zone length and for which the plastic zone length is not a substantial fraction of the critical length of the hydrided region. Thus predictions of the model for K_I close to K_{IH} and at higher temperatures are suspect because the boundary values used in the model are inconsistent with the physical situation.

There are also several other problems with Kim's model that, he claims, provides an explanation [3,5] of why the DHC rate is not affected by K_I. These assumptions are that (Kim's assumptions are in italic, the comments of this author in regular type):

(a) *There is a critical plastic zone size in the plastic zone where the hydrides can grow to a critical length, l_c, – associated with the striation spacing – that is assumed by Kim to be proportional to the square of the ratio of K_{IH} and the uniaxial yield strength.* The reason for this proportionality for the critical length, ℓ_c, for hydride cracking is not explained, but one could guess from the word 'plastic' in the definition of this zone and the form of the equation that it is analogous to the usual expression for the plastic zone length which, on the crack plane, is proportional to the square of the ratio of the applied K_I and the uniaxial yield strength. Why Kim thinks that the critical hydride length for fracture of a brittle hydrided region is given by a similar relationship to that governing the plastic zone length, or why it should depend on K_{IH} above values of applied K_I greater than K_{IH}, since the latter corresponds to a critical hydride length that is much longer and extends outside the plastic zone, is not clear to this author The association of this length with plasticity may have been made by Kim because the critical hydride length is made visible by the plastic stretch marks that are created in the more plastic matrix when the hydride fractures along its length and the crack emerges from the hydrided region. At any rate, the stated relationship, unlike that for an actual plastic zone, is a constant, depending on the ratio of two material parameters and, therefore, is independent of crack and specimen geometry and external loads. Kim provides no mechanistic justification for why the critical hydride length depends only on these material parameters and not on crack tip stress state conditions as determined by external conditions such as geometry of crack and specimen and of external loading. Such a model has, however, been provided by Shi and Puls [45,46] who presented, for the first time, a mechanistic model for K_{IH} which shows that in Stage II, where DHC is independent of K_I and the critical length is always less than the plastic zone length, the critical hydride length depends on the shape of the hydride, on the yield strength and on the hydride's fracture strength [46].

(b) *The striation spacing and the corresponding critical hydride zone length formed at the crack tip corresponds to the region over which the concentration gradient for hydrogen diffusion to the crack tip due to a difference in bulk and crack tip solvi concentrations is created.* To a first approximation there can be no hydrostatic stress gradient over the region at the crack tip where the hydrides have formed, since the nucleation and growth of hydrides is thermodynamically governed, through the dependence of the diffusion potential on the hydride interaction energy, to be driven to the highest hydrostatic stress locations. When the concentration is sufficient that hydrides precipitate there it has the effect, because of the positive misfit strain of the hydrides, to produce a region of constant and progressively decreasing hydrostatic stress [47]. Another effect of this thermodynamic driving force is that it results in the formation of a wedge-shaped hydrided region. Such a hydrided region has been experimentally observed for unfractured hydrides formed at crack tips at low K_I [19]. Experimentally it is seen that such wedge-shaped hydrided regions becomes less pronounced as the applied K_I increases. Moreover, hydride growth is always at the leading edge of such a hydrided region, so formulating a diffusion flux relationship assuming that there is a stress gradient over only this hydrided region and not between the leading edge of the crack tip hydrided region and the bulk does not make sense.

(c) *That the independence on K_I of the DHC rate experimentally observed in the range labelled Stage II, just above K_{IH}, is due to the critical plastic zone length, l_c, remaining constant*. Although experimental observations and theoretical modelling shows that the critical hydride length does become insensitive to the applied K_I when this length is less than the plastic zone length, it is not the reason for the insensitivity of the DHC rate to increases in K_I if it is assumed that the thickness of the hydride is approximately constant as it grows in length to its critical length since, with this assumption, the rate of growth of the hydride is approximately constant with time when contained within the plastic zone because the stresses in this zone are approximately constant over its length. As the fracture of the hydride is assumed to be instantaneous, it is the dependence of the diffusion rate on K_I that determines the K_I-dependence of the DHC velocity, and not the critical fracture length in this approximation. Thus when the critical hydride length is less than the plastic zone length, the stresses at the growing edge of the hydride are approximately the same regardless of the value of K_I and therefore the diffusion, and hence the DHC, rate is insensitive to K_I.

Regarding Kim's third point concerning the hydride size effect, presumably by this he means the results obtained in [48] for the difference in DHC velocity between specimens that had been furnace cooled from a temperature where all the hydrides had been dissolved and ones that had been quenched from that temperature. The different cooling treatments for the specimens would mean that the hydride sizes in the bulk would be substantially smaller in the quenched specimen compared to those in the furnace cooled specimens. Although not specifically stated in [48], the DHC velocity tests carried out by these authors were done with the temperature approached from below after these initial heat treatments. Hence these experiments are essentially similar to those carried out by Ambler [35]. Amouzouvi and Clegg [48] obtain results similar to those of Ambler, showing that the temperature at which the DHC velocity decreases with increase in temperature is higher for the quenched specimens. Thus this hydride size effect that Kim claims cannot be explained by the model falls into the same category as the second point of the claimed failure of the model, which has already been addressed in Section 5. However, it is fair to say that the explanation provided by Ambler is speculative and a definitive explanation for this interesting result remains to be determined.

The second point about the failure of the model is dealt with at length in Section 5, where it is shown that Kim is incorrect in stating that the model is incapable of explaining the effect of direction of approach to test temperature on the DHC velocity.

7. Comments on Kim's new DHC model

To correct the perceived shortcomings of the old DHC model, Kim proposed a new model [1–6]. This model is based on the postulate that the driving force for hydrogen diffusion to the crack tip hydrides is due solely to a hydrogen concentration gradient difference set up between crack tip and bulk hydrides. This concentration gradient stems from the assertion that the solvus at preferentially nucleated hydrides at the crack tip is lower than that of the hydrides in the bulk. The nucleation step of hydrides at the crack tip is postulated to occur without the aid of an increase in hydrogen concentration by diffusion there and this prior step is thought to be crucial in reducing the precipitation solvus at the crack tip to a lower value than the solvus acting at the bulk hydrides. In the following, we examine Kim's reasoning in more detail and show why his explanation is thermodynamically incorrect.

In the discussion in [4] it seems that Kim agrees that there is a dependence on stress of the chemical potential for diffusion of hydrogen in a metal (see Eq. (3) in [4]). However, he fails to see that this term, when there is a stress gradient, provides the driving force for hydride precipitation at a stressed crack under suitable conditions as demonstrated in the derivation in Section 4. Therefore he tries to demonstrate that the driving force is due to a concentration difference between the stress-affected solvus concentration at low or zero stress and that at high stress. He cites Birnbaum and co-workers' experimental results and theoretical formulation [33] for the Nb–H system as demonstrating that the solvus concentration for hydrides at the flaw is reduced by tensile stress as well as by prior plastic deformation and/or the presence of freshly nucleated dislocations. However Birnbaum and co-workers' thermodynamic relationship for the effect of stress on the hydrogen concentration at the flaw reproduced in Eq. (3) of [4] is incorrect if it is deemed to be that of the local solvus concentration since the work term for transferring the hydrogen atom from the dilute solution to the hydride (the hydrogen interaction energy) is missing from this relation. This work term is of opposite sign to the work term for forming the hydride under the same stress and would result in zero net work for the conversion if the two volume changes are of equal magnitude. The physical reason for the strong stress effect of Birnbaum and co-workers' expression for the crack tip concentration was also pointed out by Flanagan and co-workers [23] who show that the relationship given in Eq. (3) of [4] is an effective value which arises as a consequence of the effect of stress on the chemical potential of hydrogen for diffusion. The increase of hydrogen at the crack tip, driven by the thermodynamic requirement for chemical potential equalization throughout the specimen over the stress gradient, brings hydrogen to the flaw from a region of lower (or zero) stress so that when it locally transfers from the matrix to the hydride it does not figure in the local interaction energy produced compared to when the source of hydrogen in solution is that under the stress prevailing there. Another way of understanding this is that the region of highest stress at the crack tip acts as an open system in contact with a reservoir (the bulk region of the material) that has a higher (and constant, if the bulk reservoir is very large) chemical potential for hydrogen in solution than does the region at the highest stress. As a result, this region receives hydrogen from an external source at essentially zero stress (if you move the external source far enough from the highest stress region, which can always be done) and the interaction energy for it does not have to be supplied at the high stress location. This incoming hydrogen is continuously depleted as it converts to hydride at the crack tip so that the chemical potential for diffusion of the reservoir (at the bulk hydrides) always remains higher than does its corresponding value at the crack tip.

Kim, on the other hand, states [4] that the contribution of the effect of stress on the chemical potential for diffusion cannot operate as claimed because the system evolves towards a constant value of the chemical potential for diffusion throughout the region of varying stress (which is accomplished by increasing the hydrogen concentration to compensate for the increase in the value of the stress). He is correct that, as stated in Section 4, constancy of this chemical potential is a sought-for equilibrium condition for the system and will be achieved throughout the region containing the stress gradient when the concentration at the highest stress region does not exceed the solvus for hydride precipitation. However, when hydrides can form, as illustrated in Fig. 2 taken from Flanagan and co-workers' paper [23], then an inexorable sink for hydrogen exists at the hydrides there, which appears as if the hydrogen concentration there is effectively determined solely by the hydride interaction energy term given by Birnbaum and co-workers [33]. Kim fails to recognize, in claiming support for his model in Flanagan and co-workers' analysis [23], reproduced in

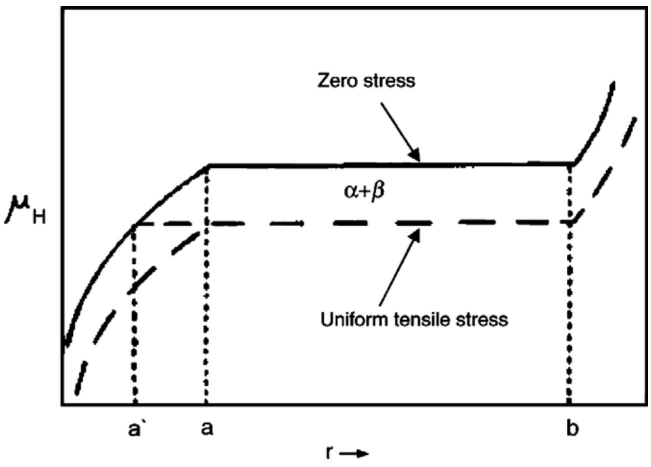

Fig. 2. Effect of stress on the chemical potentials of hydrogen in the alpha phase in zirconium for hydride precipitation (from [4] where it was reproduced from [23]). In the figure, β refers to the hydride phase, r is the concentration of hydrogen given as the ratio of hydrogen to zirconium (equivalent to x in this paper), a and b are the solvus concentrations of hydrogen in the alpha and the hydride phase, respectively, and a' is the concentration in the unstressed region at which the chemical potential of the unstressed region is equal to the chemical potential in the stressed region and is the lowest concentration in the unstressed region at which hydrides can precipitate in the stressed region.

his Fig. 4 (Fig. 2 of this paper), that this is contradictory to his criticisms of the Dutton–Puls DHC model. Flanagan and co-workers emphasize that under a uniform tensile stress in a closed system in the case when there is no volume change in converting hydrogen in solution to hydride there would be no effect of stress on the solvus as schematically indicated in Fig. 2, but this would not be the case in an open system. The lower effective concentration at the flaw tip hydride during diffusion indicated schematically in Fig. 2 is identical to that derived already in the first version of the old DHC model (the term E_ℓ in Eq. (17)). These essential features are retained in later versions of the old DHC model that include coherency strain energy and plastic work contributions to the solvi concentrations. In fact, Kim cites Puls' paper [12] on the derivation of these contributions to the solvus concentration as support for his mechanism without, again, failing to realize that accepting this result is counter to his own argument [4]. In [12], Puls shows that, when formulating the solution to the diffusion flux to the crack tip using theoretically derived values for the crack tip solvus, the resultant expression in the steady state diffusion flux solution giving the effect of stress on the precipitation solvus at the crack tip due to the hydride interaction energy is numerically approximately equal, but opposite in sign, to the hydride's accommodation or elastic strain energy, the latter being postulated as the reason why the precipitation solvus is substantially higher (in concentration) than the dissolution solvus. However, for hydrides to precipitate at the crack tip, the hydrogen concentration at the crack tip is correspondingly increased and results in hydride nucleation and growth when the magnitude of the interaction energy of the hydrogen in solution at the crack tip raises the concentration there to the value of the precipitation solvus. These balancing effects result in a total hydrogen concentration limit for DHC that is approximately equal to that of the solvus for hydride dissolution as determined in an unstressed solid. In a later evaluation of this, Shi and co-workers [39] use a different, but numerically equivalent, approach to demonstrate this approximate equivalence between the DHC concentration limit and the corresponding limit for hydride dissolution.

The foregoing analysis shows that Kim's alternative mechanism for hydrogen diffusion to the flaw tip hydride is actually not an alternative mechanism, but arises from his neglect of the interaction energy term in the chemical potential for diffusion and the presence of the stress gradient. Without the stress interaction term in the chemical potential for diffusion, the lower concentration at the flaw tip hydride relative to that at the bulk hydrides in the diffusion flux solution would not exist.

The second problem with Kim's mechanism is that, by rejecting the fact that a tensile stress gradient drives hydrogen to the crack tip, he needs to find an alternative mechanism for continually producing radial hydrides at the crack tip, since he has rejected that these hydrides could be formed there due to an increase in hydrogen concentration by diffusion produced by the action of the stress gradient. Kim claims that the first step in each DHC propagation step of repeated nucleation, growth and fracture of hydride is not the diffusion of hydrogen to the crack tip, as is implicit in the old DHC model, but the spontaneous nucleation of hydrides at the crack tip without the need to first increase the hydrogen concentration there. His qualitative explanation for this is that spontaneous nucleation is caused by the creation of plastic deformation at the crack tip at the start of each new DHC crack propagation step. As support for his claim he cites Westlake's observation [49] in the Nb–H system that when a sample was being strained during cool down up to at least 5% plastic strain the solvus temperature increased at which hydrides were observed to precipitate compared to when there was no stress applied or when the applied stress was less than the proportional limit of the specimen. Qualitatively, Westlake attributed this increase in hydride precipitation temperature as arising due to a lowering of the hydride's strain energy by plastic deformation, which was somehow aided by plastic deformation. However, at the time that this conjecture was made, actual calculations of elastic–plastic accommodation energies to demonstrate the validity of this conjecture did not exist. The work by Puls and co-workers [44] and others [50,51] has shown – at least when modelled at the elastic–plastic continuum level – that the presence of a plastic zone, by itself, would have little effect on this energy for the appropriate hydride shape. Calculations of the accommodation energies in the plastic zone of a crack for isotropically misfitting spheres, which generate large deviatoric stresses in the matrix when they form [50,51], show that some reduction of the plastic work <u>can</u> result that may be experimentally detectable, but only when the deviatoric stress, normalized to the yield strength, approaches unity, whereas for an isotropically misfitting hydride of oblate ellipsoidal shape and low aspect ratio (plate-like shape), which are shapes that are closer to those experimentally observed in DHC, there is actually a small increase in plastic accommodation [44], which is likely due to the greater amount of hydrostatic constraint generated by this shape in the matrix. Another possible effect on the accommodation energy when straining a specimen plastically during, or prior to, a solvus determination could be that this plastic straining could result in changes to the uniaxial yield strength, but this would usually produce an increase of the yield strength due to work-hardening. Increasing the yield strength would increase the accommodation energy and create an effect on the precipitation solvus opposite to what was observed by Westlake. So this second possibility could also not be the explanation for Westlake's results. Actually, Westlake [49] in the discussion of this study put more emphasis on the effect of thermal cycling under no external stress on increasing the TSSP temperature after the first thermal cycle and suggested that this is likely associated with the production of dislocation structures formed by hydrides during a prior cycle that had not been completely removed at the maximum temperature of the second cycle. This reasoning is similar to that of Pan and co-workers [30] who obtained similar effects after thermal cycling. It should be noted in the case of [30] measured on unirradiated Zr–2.5Nb pressure tube material that the highest temperature achieved for the solvus for precipitation (TSSP2) still resulted in a precipitation solvus that was well below that for dissolution (TSSD).

Moreover, Kim's claim that there is supersaturation when a new plastic zone is formed because in such a region the nucleus would be able to lower its accommodation energy, is contrary to conventional understanding [52] that, at the nucleus stage, a misfitting precipitate remains fully coherent and cannot relieve its large misfit strains because the energy barrier for the formation of dislocation loops from its surface is prohibitively large. Plastic deformation may be able to lower the bulk concentration for nucleation if the new (and previously existing dislocations) produced as a result of this deformation were able to attract hydrogen atoms to their tensile core regions in sufficient quantity. For this to happen, however, there would have to be some diffusion of hydrogen to these dislocations to bring the concentration there to just above that for the coherent solvus, so this mechanism would be similar to the diffusion process to the crack tip in the old DHC model which promotes hydride precipitation at the crack tip and which Kim has claimed is not viable. Note also that the local solvus in the tensile region of edge dislocation cores is not altered if the hydride and hydrogen interaction energies are of comparable magnitude for the same reason that it is not altered anywhere else where there are high tensile stresses, such as at a crack tip, unless there is a stress gradient that drives additional hydrogen to these centres of high tensile stress from a region of lower stress or these sites are open to external sources of hydrogen. That is, a drop in temperature alone would not result in preferential precipitation at dislocations compared to anywhere else in the solid.

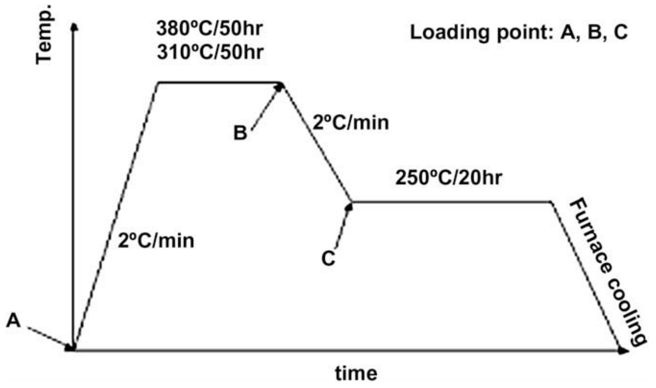

Fig. 3. Thermal cycle treatment to which the Zr–2.5Nb specimens were subjected during DHC tests (from [4]). The points A, B and C refer to when the load was applied to the specimen during the thermal cycle and correspond to the results shown in Fig. 4, labelled (a), (b) and (c), respectively.

It is also physically inconsistent to argue that nucleation of hydrides is not governed by the same effects of external stress that govern the coherent and incoherent hydride solvi. The main differences between the thermodynamic factors governing the onset of nucleation and those that govern solvus equilibrium is that the former requires some additional supersaturation, once the solvus is reached, to overcome the energy of forming a new surface, and that the nucleus can only form coherently as opposed to when the nucleus increases in size and is capable of relieving its misfit strain by plastic deformation. Both of these requirements mean that nucleation occurs at a lower temperature (or higher hydrogen concentration) when compared to the semi-coherent precipitate growth stage, or even the coherent nucleation stage and is, therefore, opposite to what Kim requires for his model to be viable.

Kim's result for the case discussed in the preceding paragraph reproduced in Fig. 4c (Fig. 5c in [4]) showing that reoriented hydrides are formed only along the crack plane support the foregoing conclusions. Note that most of the hydrides shown in the micrograph were formed from cooling after reaching 250 °C since the sample contains 60 wppm and the solvus concentration for precipitation at 250 °C is roughly 66 wppm. In case (a) in which case the load was applied at the beginning (Fig. 3) there may be some reoriented hydrides formed at 250 °C near the notch tip region due to stress amplification increasing the concentration there. With creep relaxation, the notch tip hydrides cannot crack due to a reduced local stress and likely also due to limited growth. In case (b) (Fig. 4b) DHC was initiated because the stress relaxation was now less severe. There could also be more hydrogen accumulation at the notch tip region for the same reason. In case (c) cracking was initiated at 250 °C, which then changes the stress profile from a notch to that

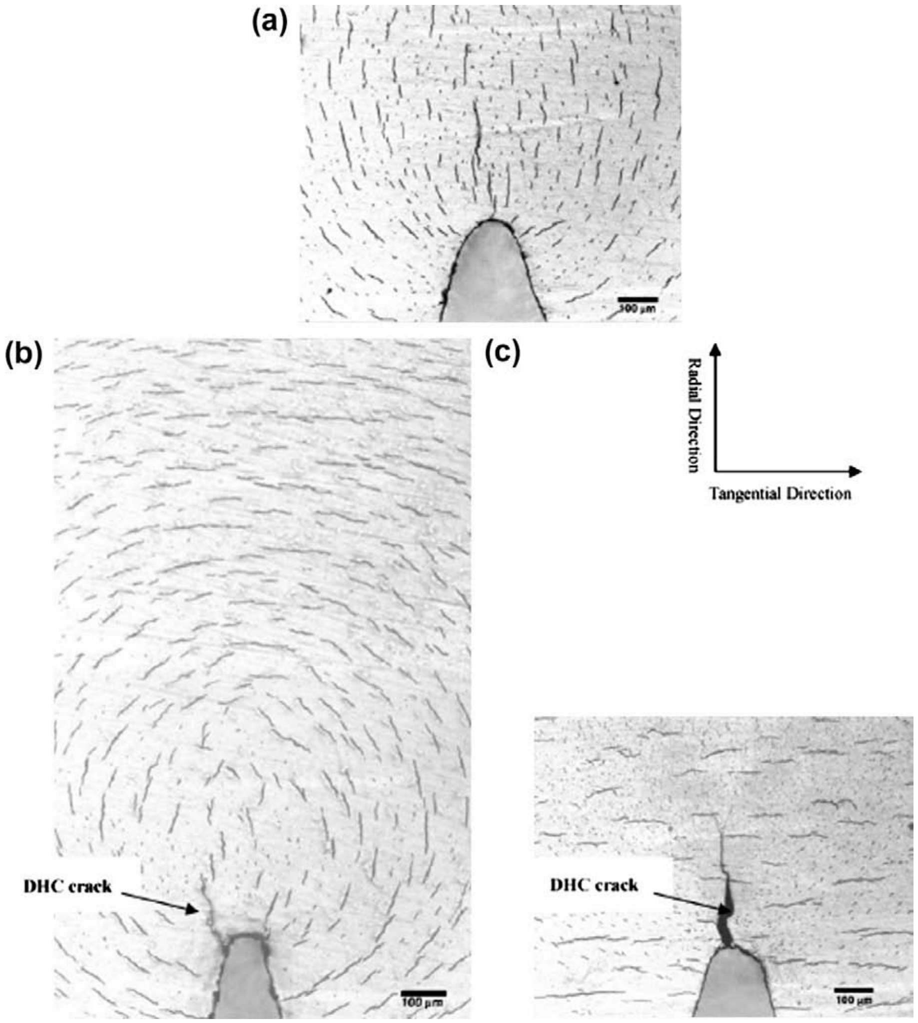

Fig. 4. Results of DHC tests (from [4]) showing the hydride distribution and DHC initiation (or not) depending on whether the load is applied (a) at A, (b) at B and (c) at C in the thermal cycle shown in Fig. 3.

of a crack, and hence few reoriented hydrides are produced around the crack except on the crack plane, which is the usual situation for constant temperature DHC.

Note that it has been experimentally demonstrated in cw Zr–2.5Nb pressure tube alloys that complete hydride reorientation is possible at an applied tensile stress of approximately 250 MPa when cooling from a temperature where all hydrides had been dissolved [53]. An applied stress of such magnitude is well below the plastic limit of the material at the temperature at which hydrides start to precipitate in these specimens, containing 60 wppm hydrogen. Therefore, prior plastic deformation is not a requirement for precipitating reoriented hydrides. This is supported by theoretical studies that show that the driving force for hydride reorientation under an externally applied stress is not plastic strain, either prior to, or during, nucleation but rather the anisotropy in the transformation strain tensor of the hydrides [54,55]. (It has also been shown in [54,55] that hydride reorientation due to external stress is only effective during nucleation.)

The foregoing discussion concerns Kim's mechanism [4] for the preferential nucleation of hydrides at a flaw during DHC when the test temperature is approached on cooling for which the hydrogen concentration in the bulk is at the solvus for hydride precipitation. DHC at constant temperature is also observed to occur (up to some maximum temperature) when the test temperature is approached by heating. Although this case can be predicted with the old DHC model as shown in Section 5, Kim proposes another mechanism [6] for preferential hydride formation at the flaw for this case to support his new DHC model. The mechanism he proposes is that the gamma hydride phase is the stable phase below 180 °C and would likely be present in the bulk in specimens of cw Zr–2.5Nb pressure tube material. (It is beyond the scope of this paper to discuss the accuracy and general validity of this claim.) Kim then claims that spontaneous nucleation of hydrides at the crack tip driven by the high stresses existing at the crack tip in this temperature range would favour the formation of delta hydride nuclei (or the conversion of previously nucleated gamma hydrides to delta; it is not clear from his description which case he means) because, he claims, the tensile stresses acting there would favour the formation of this phase below 180 °C. Other than his observations (and those of others) that the hydrides growing at the crack tip during DHC are of the delta phase, he provides no quantitative mechanistic explanation for the validity of this assertion. Now, having assumed that delta hydride nuclei have formed at the crack tip and at least some gamma hydrides are present in the bulk, the driving force for diffusion of hydrogen to the crack tip hydride for this case is based on the premise, supported by limited experimental data, that the gamma hydride solvus concentration for hydride dissolution is higher than that of the delta hydride solvus.. (It should be noted that the X-ray diffraction analyses results given in [4] that are cited by Kim as support for the presence of gamma hydride in the bulk appear to this author to be not very convincing.) As a result there would be a flow of hydrogen to the stress-stabilized delta hydride nuclei at the crack tip, causing them to grow to their critical size for fracture. This could only happen if the hydride solvus for precipitation for delta hydrides had attained a stress-assisted value that would be less than that of the solvus for dissolution of the gamma hydrides in the bulk. This difficulty in the workability of his model aside, the assertion of a higher solvus concentration for gamma dissolution compared to that for delta hydride dissolution is highly speculative.

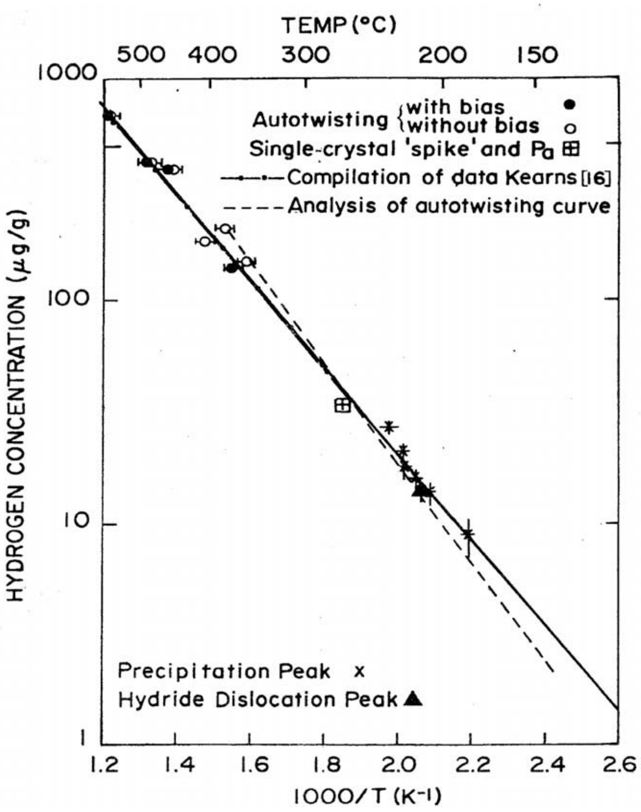

Fig. 5. Hydrogen solvus concentration as a function of reciprocal temperature for the TSSD data obtained by Ritchie and Sprungmann [57] compared with compilation by Kearns (J.J. Kearns, J. Nucl. Mater. 22 (1967) 292) reproduced from [57].

To begin with, it is known that there are differences in solvi concentrations depending on the yield strength of the alloy and the presence and extent in the alloy of the beta phase. Secondly, the various detection methods can result in differences ranging over more than 10 K in the solvus concentration for a given concentration depending on the method and the criteria used to determine when the terminal solubility has been reached. For instance, there are various views expressed in the literature as to which is the appropriate criterion to use to determine the terminal solubility when using the DSC method [56]. Also the work of Ritchie and Sprungmann [57] concludes that "... *the data on the TSS boundary given in Fig. 12* [reproduced in this paper as Fig. 5] *agree well with those of other workers. In the high temperature range, the data are close to the compilation reported by Kearns. In the lower temperature range, the results are within the limits of the data reported by Cann and Atrens* [Ref. [58] in this paper]." Ritchie and Sprungmann further state that "...[Cann and Atrens] *have suggested that the data at high temperature contents correspond to the δ-phase boundary, while those at lower hydrogen contents correspond to the metastable γ-phase boundary. If this is the case, then the results in Fig. 12* [reproduced as Fig. 5 in this paper] *show that, within experimental error, both boundaries can be described by the same solubility equation.*". Regarding the data by Mishra and Asundi [59], Ritchie and Sprungmann conclude that "*It should be noted that the results in the low temperature range do not agree with the IF results reported by Mishra and Asundi* [Ref. [59] in this paper]. *It is difficult to understand why these authors did not observe the precipitation peak with their very fast cooling rate, unless their soaking temperatures were already on the low temperature side of the precipitation peak. This appears to be the case in the representative data given in their paper and explains why their estimation of the TSS boundary is at a much lower temperature for a given hydrogen content than the data in Fig. 12.*" In addition, the accuracy of terminal solubility data at H concentrations below about 10 wppm is reduced because of reduced signal strengths in the various techniques used to detect the terminal solubility and because of the difficulty of getting reliable chemical measurements of H at such low concentrations. It is also for this reason that there are so few data points in the low H/low temperature region. Considering the uncertainties in the data, then, it helps to interrogate the data on the basis of physical expectations derived from other methods, one of which would be first-principles calculations of the H–Zr binding energy such as those by Domain and co-workers [60] that would give an estimate of whether a significant difference in the chemical part of the enthalpy of formation would prevail between the two hydride phases (i.e., the part of the enthalpy that is separate from the accommodation energy and which just accounts for the various binding energies (H from the gas phase to the dilute solution and from there to hydride)). This calculation shows that the binding energies of the two hydride phases are similar and therefore that the chemical component of the enthalpy of hydride formation is the same for both phases. Given this result, and that the accommodation energy of the gamma phase is less than that of the delta one [8,9,61], leads to a theoretical prediction for the solvus concentration for the gamma phase which is slightly less than that for the delta phase. These theoretical results suggest that there may be other interpretations for the presence of the gamma phase at low temperature and also for the various persistent indications by some in the literature that the solvus line has a different slope below about 200 °C.

Kim's model, as indicated in the preceding paragraphs, hinges crucially on a number of factors: one is that the gamma phase is the stable phase below 180 °C; the second is that the thermomechanical history of the sample was such that it has resulted in them actually being present in the bulk, and the third is that it has a higher solvus compared to that of the stress-stabilized delta phase. It also hinges on, presumably, the same mechanism for spontaneous nucleation and for reducing the solvus at the crack tip from the stress-unaffected TSSP to a magnitude equivalent to that for a stress-unaffected TSSD although this is not pointed out in [6]. The spontaneous nucleation mechanism was shown to be a physically improbable one in the preceding section. It is also puzzling that the gamma phase would be the stable phase if it were to have a higher solvus concentration (at a given temperature) than that of the delta phase, since the delta phase's solvus would be reached first on cooling. In addition, if gamma were the stable phase at lower temperature, then a solvus concentration of H in the zirconium matrix for the delta phase would be meaningless as it would be to the left of the gamma phase in the phase diagram and it could only have a solvus with respect to the gamma phase on the low-hydrogen side of the phase diagram. Kim cites the explanation by Nath and co-workers [62] that the reason that the metastable gamma phase would form in favour of the delta one at high cooling rates could be due to a lower solvus temperature (i.e., higher solvus concentration) for the gamma versus the delta phase. However, these authors presented data that convinced them that the gamma phase is a metastable one and their explanation in terms of the difference in solvi was simply a speculation of one reason why the metastable gamma phase might form in favour of the delta when cooling quickly to ambient temperature. It is more likely that the reason is associated with differences in kinetic requirements (the gamma phase contains fewer H/Zr atoms to form) during rapid cooling that could compensate for the likelihood of a higher surface energy for the gamma phase when it nucleates.

8. Conclusions

1. A review of the thermodynamic foundation of the model for the rate of DHC propagation first developed by Dutton and Puls and referred to as the old model in this paper has shown that it has properly accounted for the effect of stress on the chemical potential of hydrogen for diffusion and for two-phase equilibrium in metal–hydrogen systems and, specifically, in zirconium alloys. In particular this review has reiterated the previously made assertion that hydride precipitation and growth to fracture at the tip of a flaw under tensile stress, and hence DHC, occurs primarily due to stress-driven flow of hydrogen to the crack tip. This conclusion counters recent assertions by Kim and co-workers that this is not the mechanism of DHC and that, therefore, the old model is faulty and a new model would need to be formulated.
2. A review of the literature on this subject has shown that there have been occasionally incorrect or ambiguous statements [7,8,18,38] – including by this author – regarding the physical origins of the flux of hydrogen to the crack tip resulting in hydride precipitation and growth. The most important of these statements is the assertion that the concentration difference driving diffusion of hydrogen to the crack tip making DHC possible is the result of a significant reduction of the solvus concentration due to external tensile stress. Although the thermodynamic formulation has shown that there can be such a concentration difference when there is a net volume change on converting a portion of the dilute alpha zirconium phase to hydride, this effect is not significant in most metal–hydrogen systems including zirconium alloys, as the net volume change is small and therefore would not be sufficient to result in DHC. It is shown, in fact, that DHC is possible almost solely due to the effect of stress on hydrogen in solution. This demonstrates the necessary role played by the stress gradient and its effect on the chemical potential of hydrogen for diffusion in making DHC possible, contrary to the assertions by Kim and co-workers that it plays no role.
3. The new model developed by Kim is qualitative and, being highly simplified, contains no explicit formulations of the thermodynamic boundary conditions needed to solve for the diffusion flux for precipitation and growth of hydrides at a flaw. It is based on the claim that hydrogen diffusion to the crack tip is driven solely by a concentration difference produced due to a claimed strong effect of stress on the solvus concentrations between hydrides in the bulk and at the crack tip. This view is a consequence of the erroneous conclusion by Kim that the stress gradient effect given in the old model would not result in a diffusion flux of hydrogen to the crack tip because this effect results in a chemical potential for hydrogen for diffusion that, at equilibrium, has a constant value in the region between the bulk and crack-tip hydrides. The error made in this formulation is in neglecting to account for the volume change resulting from the transfer of hydrogen from solution in the alpha zirconium phase to the hydride phase, the transfer of which is a requirement when converting the dilute alpha zirconium phase to hydride. When this error is corrected, it is seen that, in a stress gradient, there can be no equilibrium between hydrides under different external stress values, which is the reason that the claimed constancy of chemical potential for diffusion cannot be possible in this case.
4. A possible reason for the confusion by Kim and by others made in the past regarding the physical origin of the preferential growth of hydrides at the high stress side of a stress gradient may be that the solution of the steady state arrival rate of hydrogen to the crack tip in the old model (and subsequent refinements of it) results in a hydrogen arrival rate that is proportional to the difference in concentrations between bulk and crack tip hydrides that appears as though the externally unstressed solvi concentrations at the two locations have been substantially reduced by stress. The reason for this result has been explained as being a consequence of the action of the effect of the stress gradient on the chemical potential for diffusion of hydrogen.

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Appendix A. Moutier cycle under external stress and full coherency stresses

(Derivation for hydride solvus as affected by coherency and external stresses; revision of version given in [11].)

Step 1: Transfer δn moles of hydride from n moles of hydride phase to solution phase ($x \cdot \delta n$ moles of H and δn moles of Zr, given that the hydride phase has composition ZrH_x). The system is in equilibrium under external and coherency stresses at chemical potential, μ_H^{s,coh,σ^A} with corresponding solvus concentration in the solution phase, c_H^{s,coh,σ^A}. Therefore the work, W_1, required to carry out this transfer is zero because the system is in equilibrium.

$$W_1 = 0 \tag{A.1}$$

Step 2a: Excise the remaining $(n - \delta n)$ moles of hydride, but maintain the external stresses on the solution phase. The work required, W_{2a}, is the reduction in coherency stresses in matrix and hydride and increase in external work due to removal of the hydride phase from the external stress.

$$W_{2a} = -w_t^{inc} - w_t^a \tag{A.2}$$

w_t^{inc} is the hydride–matrix strain energy and w_t^a the interaction energy (negative for tensile external stresses).Only the interaction energy with the hydride is removed here because the external stress is still acting on the hydrogen in solution, although it no longer has the coherency stresses of the hydride acting on it.

Step 2b: Remove external stresses. The work required, W_{2b}, is:

$$W_{2b} = W_L - W_E \tag{A.3}$$

W_L is the energy of loading system and W_E the elastic energy of system.The chemical potential, $\mu_H^{s,o}$, which is the potential for the hydrogen in the solution phase in equilibrium with an unstressed hydride, is increased by $p \cdot \overline{V}_H$ because there is no change in H concentration in the solution phase when removing the stress.

Step 3: Transfer δn moles of hydride to the relaxed, externally unstressed hydride by transferring $x \cdot \delta n$ moles of H and δn moles of Zr from the relaxed, unstressed solution phase. This requires chemical work, W_3, as follows:

$$W_3 = \left(\mu_H^{s,o} + p \cdot \overline{V}_H - \mu_H^{s,coh,\sigma^A}\right) \cdot x \cdot \delta n \tag{A.4}$$

The chemical work arises because, the equilibrium chemical potential for the transfer in Step 3 is that given by $\mu_H^{s,o} + p \cdot \overline{V}_H$ whereas the chemical potential in the system is actually at μ_H^{s,coh,σ^A}.

Step 4a: Replace the external stress. The work for this step is:

$$W_{4a} = -W_L + W_E \tag{A.5}$$

Step 4b: Replace hydride coherently into previously relaxed cavity created when hydride was cut out in Step 2a. The work, W_{4b}, is:

$$\begin{aligned} W_{4b} &= w_t^{inc} + w_t^a + \frac{\partial w_t^{inc}}{\partial n} \cdot \delta n + \frac{\partial w_t^a}{\partial n} \cdot \delta n \\ &\equiv w_t^{inc} + w_t^a + \bar{w}_t^{inc} + \bar{w}_t^a \end{aligned} \tag{A.6}$$

where the first two terms refer to the work in replacing the $(n - \delta\ n)$ moles of hydride that was excised in Step 2a and the second two terms refer to the additional δn moles that are added in this step and where

$$\bar{w}_t^a = -\frac{\overline{V}_{Zr}}{x} \cdot \sigma_{ij} \cdot e_{ij}^T \tag{A.7}$$

Summing the work contributions given by Steps 1 to 4b to zero yields (after cancelling identical terms of opposite sign and dividing the remaining terms by δn):

$$\left(\mu_H^{s,o} - \mu_H^{s,coh,\sigma^A} + p \cdot \overline{V}_H\right) \cdot x + \bar{w}_t^{inc} + \bar{w}_t^a = 0 \tag{A.8}$$

Transposing terms, yields:

$$\mu_H^{s,coh,\sigma^A} = \mu_H^{s,o} + p \cdot \overline{V}_H + (\bar{w}_t^{inc} + \bar{w}_t^a)/x \tag{A.9}$$

Since for low H concentration in the dilute phase

$$\mu_H^{s,coh,\sigma^A} \cong RT \cdot \ell n(c_H^{s,coh,\sigma^A}) \tag{A.10}$$

$$\mu_H^{s,o} \cong RT \cdot \ell n(c_H^{s,o}) \tag{A.11}$$

then the coherent, externally stressed solvus concentration in the dilute phase, c_H^{s,coh,σ^A}, is given in terms of the solvus concentration in the incoherent, externally unstressed dilute phase, $c_H^{s,o}$, by:

$$c_H^{s,coh,\sigma^A} = c_H^{s,o} \cdot exp\left[(\bar{w}_t^{inc} + \bar{w}_t^a)/xRT\right] \cdot exp(p \cdot \overline{V}_H/RT) \tag{A.12}$$

The foregoing result is for the case of hydride dissolution in Step 1. However, the same result is obtained by starting with hydride precipitation in Step 1 since the sign of δn is reversed placing a negative sign in front of Eq. (4) and in front of $\bar{w}_t^{inc}$ and $\bar{w}_t^a$ in Eq. (A.6), which cancels out the effect of this sign change in the final result.

Appendix B. Numerical evaluation of terms affecting solvus concentration under stress

In [10], it is shown that under a uniform stress the solvus concentration for hydride precipitation is given in terms of the solvus concentration for hydride precipitation under zero stress as follows:

$$c_H^s(p) = c_H^s(0) \cdot exp\left\{\left[p^{flaw} \cdot \overline{V}_H + \bar{w}_t^a\right]/RT\right\} \tag{B.1}$$

where[2]

$$\bar{w}_t^a = -\frac{\overline{V}_{Zr}}{x} \cdot \sigma_{ij} \cdot e_{ij}^T \tag{B.2}$$

and $\overline{V}_{Zr}$ is the partial molar volume of zirconium, σ_{ij} the applied stresses, e_{ij}^T the stress-free transformation strains to transform Zr to zirconium hydride, x the composition of hydride phase (ZrH_x), p the hydrostatic stress and p^{flaw} the hydrostatic stress at flaw

In this section a numerical comparison is made of the net interaction energy in the exponential in Eq. (B.1), using the bounding values for the transformation strains.

To determine the magnitude of the net interaction energy, we assume that we have applied stresses σ_{11}, σ_{22}, σ_{33} in the through-wall, axial and transverse directions, respectively, of the pressure tube. The coordinate system for the stresses has been chosen such that for a flaw oriented with the fracture plane for DHC initiation and propagation oriented in the radial/axial direction of

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[2] In [10], $\bar{w}_t^a$ is incorrectly expressed in terms of $\overline{V}_{hyd}$, the partial molar volume of zirconium hydride per mole H.

the pressure tube, the hydride platelet normal would be oriented in the transverse (σ_{33} direction). Using the data given in Appendix C, this gives

$$p^{flaw} \cdot \overline{V}_H = \overline{V}_{Zr} \cdot (\sigma_{11} \cdot 0.033 + \sigma_{22} \cdot 0.033 + \sigma_{33} \cdot 0.054) \tag{B.3}$$

For consistency with the hydride interaction energy formulation in this illustration the hydrogen molar volume has been expressed in terms of its misfit stresses with reference to the molar volume of the Zr lattice in which it forms. The misfit strains measured by McEwen and co-workers (see Appendix C) have been used[3]. This reduces to an effective isotropic hydrogen molar volume of 1.68×10^{-6} m^3/(mol H), very close to the hydrogen molar volume used in most other evaluations.

For the case of a <u>pure lattice strain transformation</u>, the hydride interaction energy for the delta phase is:

$$\bar{w}_t^a = -\frac{\overline{V}_{Zr}}{1.5} \cdot (\sigma_{11} \cdot 0.0486 + \sigma_{22} \cdot 0.0486 + \sigma_{33} \cdot 0.0748). \tag{B.4}$$

Combining Eqs. (A.3) and (A.4), the net interaction energy becomes:

$$\frac{\bar{w}_t^a + p^{flaw} \cdot \overline{V}_H}{RT} = \frac{\overline{V}_{Zr} \cdot (\sigma_{11} \cdot 0.0006 + \sigma_{22} \cdot 0.0006 + \sigma_{33} \cdot 0.00413)}{RT} \tag{B.5}$$

Substituting this result into Eq. (B.1) yields:

$$c_H^s(p) = c_H^s(0) \cdot exp\left\{\frac{\overline{V}_{Zr} \cdot (\sigma_{11} \cdot 0.0006 + \sigma_{22} \cdot 0.0006 + \sigma_{33} \cdot 0.00413)}{RT}\right\} \tag{B.6}$$

As a numerical example, for a crack, assume [10]:

$$\sigma_{11} = 2.71 \cdot \sigma_y, \quad \sigma_{22} = 2.08 \cdot \sigma_y, \quad \sigma_{33} = 3.35 \cdot \sigma_y$$
$$\sigma_y = 1088 - 1.02 \cdot T\ (\mathrm{K})$$
$$T = 250\,^\circ\mathrm{C}\ (523\ \mathrm{K})$$
$$\overline{V}_{Zr} = 14.0024 \times 10^{-6}\ \mathrm{m^3/(mol\ Zr)}$$

Evaluating Eq. (B.6) with the data above yields:

$$c_H^s(p) = c_H^s(0) \cdot exp\left\{\frac{129\ \mathrm{J/mol\ H}}{RT}\right\} \tag{B.7}$$

This result shows that there is a negligible effect of uniform stress on the solvus for the case where the hydride transformation strain is a pure lattice strain.

For the case of an <u>invariant plane strain transformation</u>, the only normal transformation strain for the hydride is that acting normal to the hydride plate which must be equal to the total volume change for the transformation [43]. Hence, the hydride interaction energy is:

$$\bar{w}_t^a = -\frac{\overline{V}_{Zr}}{1.5} \cdot (\sigma_{33} \cdot 0.172) \tag{B.8}$$

Combining Eqs. (B.3) and (B.8) yields:

$$\frac{\bar{w}_t^a + p^{flaw} \cdot \overline{V}_H}{RT} = \frac{\overline{V}_{Zr} \cdot (\sigma_{11} \cdot 0.033 + \sigma_{22} \cdot 0.033 - \sigma_{33} \cdot 0.06)}{RT} \tag{B.9}$$

Evaluating the stresses at the crack using the data above and substituting the result into Eq. (B.1) yields:

$$c_H^s(p) = c_H^s(0) \cdot exp\left\{\frac{-333\ \mathrm{J/mol\ H}}{RT}\right\} \tag{B.10}$$

This result shows that for an invariant plane strain transformation the net interaction is similar in magnitude but of opposite in sign to that obtained for the pure lattice strain case.

Therefore, for the two bounding cases of the hydride's possible transformation strains, the effect of stress on the solvus is predicted to be undetectably small compared to the usual scatter in the data, even at the elevated stresses existing at a crack tip.

Appendix C. Numerical values for the parameters in the hydride/hydrogen interaction energy expressions

Converting a volume of Zr to zirconium hydride, for which the volume change is relatively small, and assuming without loss of generality that it is a parallelopiped having lengths 'x_1', 'x_2', 'x_3', we can approximate this change as follows:

$$\begin{aligned} V(Zr) + \Delta V(Zr \to ZrH_x) &= (x_1(Zr) + \Delta x_1(Zr \to ZrH_x)) \\ &\quad \cdot (x_2(Zr) + \Delta x_2(Zr \to ZrH_x)) \\ &\quad \cdot (x_3(Zr) + \Delta x_3(Zr \to ZrH_x)) \end{aligned} \tag{C.1}$$

Dividing by $V(Zr)$ and rearranging terms yields

$$\begin{aligned} \Delta V(Zr \to ZrH_x) = V(Zr)(&e_{11} + e_{22} + e_{33} + e_{11} \cdot e_{22} + e_{11} \cdot e_{33} \\ &+ e_{22} \cdot e_{33} + e_{11} \cdot e_{22} \cdot e_{33}) \end{aligned} \tag{C.2}$$

$$\text{where the strains } e_{ii} = \frac{\Delta x_i}{x_i}, \quad i = 1, 2, 3 \tag{C.3}$$

are the equivalent of the stress-free transformation strains, e_{ii}^T, given in the $\bar{w}_t^a$ expression.

For small strains it is sufficiently accurate to retain only the first order terms, yielding

$$\Delta V(Zr \to ZrH_x) = V(Zr)(e_{11} + e_{22} + e_{33}) \tag{C.4}$$

The partial molar interaction energy, $\bar{w}_t^a$, is the dot product of the partial molar value of the volume change matrix, given by Eq. (C.4), with the stress matrix. Eq. (C.3) also demonstrates that the partial molar volume of zirconium is the appropriate volume in this expression. Values for the partial molar volume of Zr, the composition of the hydride phase that has formed, and its misfit strains, e_{ij}^T, etc. are required for numerical evaluation.

Carpenter [40] has derived values for the misfit strains of delta and zirconium hydride. The values calculated have been derived on the basis of Eq. (C.2) for the volume change. For delta hydride, he obtains $e_{11}^T = e_{22}^T = 0.0458$ and $e_{33}^T = 0.072$ where the directions are with respect to a plate-shaped hydride with its plate normal direction, x_3, oriented approximately in the [0001] (basal pole or $\langle c \rangle$) direction of the surrounding hexagonal close-packed Zr matrix and the other two directions are perpendicular to this and orthogonal to each other in the plane of the plate. Substituted into Eq. (C.2), they yield an overall volume change for delta hydride of 17.2%. To ensure that the same volume change is obtained using the truncated volume change expression of Eq. (C.4), which is used in $\bar{w}_t^a$, one approach is to increase each misfit strain by 0.0028, giving $e_{11}^T = e_{22}^T = 0.0486$ and $e_{33}^T = 0.0748$ for delta hydride. A similar approach could be employed if gamma hydride were assumed to be the hydride that is precipitated. In previous calculations of $\bar{w}_t^a$ given in the literature (e.g., Ref. [10] and the references cited therein), the misfit strains quoted by Carpenter [40] were used as was the molar volume of zirconium hydride instead of zirconium.

An important parameter in $\bar{w}_t^a$ is the composition of the hydride phase. Carpenter [40], citing [63], gives the composition of delta hydride to be $ZrH_{1.66}$ and this was given to be the composition of delta zirconium hydride in most publications dealing with DHC. A re-examination of the literature, however, suggests that hydride which is formed in the temperature range that is of interest for

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[3] Note that MacEwen and co-workers quote an equation for the effect of stress on the solvus (their Eq. (6)) which appears to have used the same sign convention for p as that used by Dutton and Puls [7]. With the conventional sign convention for p, the signs for the two hydrogen volumes should be reversed.

hydride formation in pressure tubes has a range of values from 1.47 to 1.59 from 300 °C to ambient, respectively (e.g., as cited by Beck [64]). A value of $x = 1.5$, seems to be a sensible choice at this stage. Note that, similar to the solvus concentration, x varies with temperature, except that it decreases with increasing temperature, the opposite to the solvus concentration. Also whether hydride is forming or dissolving should affect x qualitatively in the same way that it affects the solvus concentration (i.e., it should be different depending on which process is occurring), but the magnitude of this effect, if any, has not been determined. Regarding the gamma hydride phase, it is generally accepted that it is a metastable phase, having composition ZrH, i.e., having exactly half the available tetrahedral sites in the lattice occupied by hydrogen atoms. Hence, for this phase, $x = 1$. There is still uncertainty in the literature under what conditions gamma hydride forms and whether this phase plays a significant role in DHC.

In addition to the misfit strains and composition of the hydride, the molar (or atomic) volume of the Zr lattice is required to evaluate $\bar{w}_t^a$. Carpenter [40], using lattice parameter values measured at ambient temperature, cites an atomic volume of $\Omega_{Zr} = 2.326 \times 10^{-29}$ m^3/atom, which, after multiplying by Avogadro's Number converts to $\overline{V}_{Zr} = 14.0024 \times 10^{-6}$ m^3/(mol Zr). McEwen and co-workers [65] derive a value of Ω_{Zr} of 2.352×10^{-29} m^3/atom based on their lattice parameter measurements at 454 °C. This shows that Ω_{Zr} increases slightly with temperature. Since the exact temperature dependence of Ω_{Zr} is not available, we will use the value at room temperature.

For the hydrogen molar volume, $\overline{V}_H$, a value of 1.67×10^{-6} m^3/(mol H) has generally been used, assuming that the misfit is isotropic. In fact, the misfit is tetragonal. It was measured at 477 °C by McEwen and co-workers [65] to have strains of 0.054 in the $\langle c \rangle$ direction (e^T_{33}) and 0.033 in the $\langle a \rangle$ directions (e^T_{11}, e^T_{22}). Using the room temperature value of Ω_{Zr}, assuming that temperature affects only this volume and not the strains, yields $\overline{V}_H = 1.68 \times 10^{-6}$ m^3/(mol H), in close agreement with the value generally used.

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