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Review

Comments on author's reply to "Review of the thermodynamic basis for models of delayed hydride cracking rate in zirconium alloys", M.P. Puls in J. Nucl. Mater. 393 (2009) 350–367

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A R T I C L E I N F O

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A B S T R A C T

This work comments on Kim's rebuttal of this authors' critical review that is cited in the title of this paper. The author shows that Kim's rebuttal of the author's review is based on essentially the same physical misconceptions concerning the driving force for DHC rate in the Dutton–Puls model as are given in Kim's original papers. The author shows that his previous criticisms of Kim's model as well as the author's defense of the correctness of the thermodynamic basis of the various versions of the Dutton–Puls models have been validated. In contradistinction, the author shows that it is Kim's DHC model that has a faulty thermodynamic basis and, therefore, is not viable in underpinning the physical understanding of DHC rate. To make the reasons for these conclusions clearer than given previously, the author has attached an appendix to these comments that provides detailed steps of the mathematical derivations of the various versions of the Dutton–Puls models. This work also provides an interpretation of the results of the experiments of Kammenzind et al. (2000) [5] that shows that these results can be interpreted according to the Dutton–Puls mechanism for hydride growth. Thus the results of the Kammenzind and co-workers' tests do not provide support, as Kim claims, that a stress gradient in a closed system cannot cause hydrogen concentration redistribution.

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1. Introduction

The purpose of this note is to reply to Kim's rebuttal [1] of this author's criticisms [2] of Kim's DHC rate model. It is demonstrated that Kim's rebuttal is based on the same erroneous concepts that Kim has made in his published papers. In the following we address Kim's comments according to the sections in which they appear. Wording used by Kim is written in italic font and enclosed by quotation marks.

2. Comments on Section 2: Comment on the old DHC model

2.1. Comments on Section 2.1: Driving force for hydrogen diffusion

In this section Kim repeats his criticism of the original Dutton–Puls model, citing for its limitations that it requires the presence of hydrides in the bulk. In addition he also still seems not to realize that the DHC rate expression derived is an analytic solution of a steady-state diffusion equation. It seems the reason that Kim concludes that the Dutton–Puls steady state flux result is not the solution of a diffusion equation is because the resulting expression has a similar form as does his own. In Kim's case the solution is simply given as the finite difference between crack tip and bulk solvi concentrations divided by the distance over which this concentration gradient acts. Kim also continues to have the perception that subsequently developed models by this author have different physical bases. To explicitly demonstrate that this is not the case, the author has summarized the details of the mathematical derivation of the original Dutton–Puls model plus all subsequent modifications to it in Appendix A. It is pointed out in Appendix A that in the original Dutton–Puls model it was assumed that hydrides must be present in the bulk because that is what the early results appeared to show, but also because it assured the constancy of the hydrogen concentration in the bulk (at $r = L$) when hydrides are present, since these hydrides can act as a large reservoir of hydrogen to replenish the hydrogen in solution that would continually flow to the crack tip. This then assured the validity of the steady state assumption that led to the solution of the diffusion flux, (Eq. (A24) in Appendix A). However, as McRae and co-workers have indicated [3], it is probably not a bad approximation to assume that there would be little change in the bulk hydrogen concentration in solution even when it is not being replenished by dissolution of hydrides there. Hence, the concentration in the bulk, at $r = L$, could have different values depending on the most recent thermal–mechanical history of the material prior to reaching the test temperature conditions and depending on the total hydrogen content in the system. Upon making this change to the boundary conditions applied in the Dutton–Puls model, plus taking account of the hysteresis in the solvi concentrations, all of the claimed limitations of the Dutton–Puls model that were stated by Kim to be proof that the model is inadequate, are eliminated. This is further supported by the recent comparison of the numerical predictions of the model with a large number of previous, as well as more recent, experimental results [3]. (It should be noted that McRae and co-workers refer to their DHC propagation rate model as a Diffusion First Model (DFM) suggesting that it is a refinement of the original Dutton-Puls model, the latter of which they claim is flawed because it requires there to be an effect of stress on the solvi for the latter model to predict that DHC propagation is possible. This assertion is incorrect. A simple substitution of their chemical potential terms for hydrogen diffusion, $\mu^0(r)$, $r = a$ and b at the crack tip and in the bulk of the solid, respectively, by the corresponding work terms $p(r)\cdot V_H$, where p is the pressure at position, r, from the crack tip and V_H the hydrogen formation volume shows that the DFM is identical to the Dutton-Puls model. It should also be noted that they incorrectly refer to these chemical potential terms as arbitrary reference potentials when they are, in fact, chemical potential expressions for the effect of stress on hydrogen relative to some reference chemical potential state usually taken to be that of the stress-free solid and written, μ^0.)

Kim states that the original Dutton–Puls DHC rate expression (his Eq. (1)) is not an analytic solution of the diffusion equation by claiming that "*…the so-called analytical model as claimed by the author* [1] [Ref. [2] in this paper] *has nothing but the theoretical calculations of hydride solubility at the crack tip and in the bulk…*". It is shown in Appendix A that this is not true and that what Kim claims are the hydride solubilities at the crack tip and in the bulk (i.e., the solvi) are, in fact, not hydride solubilities or solvi, but rather relative sink strength concentrations that take the form they do in the steady-state diffusion equation solution because of the effect of the stress gradient in the diffusion equation. A step-by-step derivation of the solution to the diffusion equation is also given in Appendix A, which clearly demonstrates that Kim's foregoing assertion that the result is not an analytical model is incorrect.

Kim then points out that "*As it was later known that the stress produced no change in hydrogen interaction energy due to little change in the molar volume of hydrogen between the zirconium and the hydride, causing no change in the hydrogen solubility between the bulk and the crack tip, the author had to derive the revised model using the hydride interaction energy rather than the hydrogen interaction energy*". Here Kim gets his chronology (and causality) reversed, since the use of the hydride interaction energy rather than the hydrogen-in-hydride interaction energy predates the experimental finding that the hydrogen molar volumes in matrix and hydride are numerically approximately equal. This is also explained in Appendix A.

Kim's misconception regarding the Dutton–Puls model and its later variations all stem from not having apparently gone through the derivation of that model in detail, since, otherwise he would have seen that the theoretical boundary bulk and crack tip solvi expressions correctly account for the effect of applied stress. All of Kim's subsequent criticisms of the Dutton–Puls model stem from these foregoing misconceptions.

Another of Kim's misconceptions is that the test specimen is a closed system "*…because hydrogen cannot enter into or come out of the zirconium matrix*" for which, ironically, he cites [4]. However, as is pointed out in [1], Flanagan and co-workers' analysis actually implicitly supports this author's model. This support is found in their section on the effect of non-uniform (this author's underlining) stress on hydride precipitation. Note that a solid in which a stress gradient is introduced (say, by introducing a crack, or a dislocation), even though it may otherwise be closed to the external world, is internally an open system over the stress gradient. The hydrogen concentration in such a system containing an internal stress gradient would be able to adjust itself (subject to the mass balance constraint of constant overall hydrogen content in the solid) so that, at equilibrium, the chemical potential would have the same value throughout the solid (if no hydride is formed to act as a sink for hydrogen). This is also the reason why, for instance, misfitting point defects (impurity atoms (substitutional or interstitial), vacancies and self-interstitials) migrate to edge dislocations.

Kim uses a closed milk container analogy, and the need to pressurize it to draw out the milk with a straw, to support his claim that the specimen containing a crack under stress is a closed system. It is worth pointing out some of Kim's misconceptions regarding this analogy. He suggests that pressurizing the milk container in a closed system containing hydrogen in solution is equivalent to applying a cooling thermal cycle on the specimen because "*…to pull hydrogen toward the crack tip under tensile stresses, shrinking the bulk of the zirconium matrix by cooling is required to squeeze hydrogen in solution in the bulk. Evidence is provided by Kammenzind's experiment* [19] [reference [5] in this paper] *where* *no transfer of hydrogen was seen between the stressed regions and the unstressed regions in an isothermal condition when the Zircaloy-4 plates with the same concentration along the length was held at 371 °C for 50 days followed by cooling to room temperature under constant stress. However, after 25 thermal cycle treatments with cooling from the peak temperature, the stressed region had a higher concentration than the unstressed region due to precipitation of hydrides in the stressed region under cooling.*"

The reason for not observing a change in concentration between the stressed and unstressed region in Kammenzind and co-workers' experiments [5] under isothermal conditions is that the stress difference between the two regions in these experiments was too small for there to be a sufficiently large concentration difference that would be detectable given the 5% uncertainty in the hydrogen concentration measurement method. In contrast, under thermal cycling conditions, with the hydrogen content in the samples above the solvus at the maximum temperature, the small amount of extra hydrogen migrating during the high temperature hold to the stressed region would be precipitated as hydrides during the subsequent cooldown, not all of which would redissolve during the temperature increase to the maximum temperature in each thermal cycle under stress due to the difference in stress between the two regions and the hysteresis in the solvus. Hence, this ratcheting mechanism resulted in a progressive increase in the volume fraction of hydrides in the stressed region that translated into a substantial measurable difference in hydrogen concentration between the stressed and unstressed regions of the sample after 25 thermal cycles. Kammenzind and co-worker interpreted their result theoretically as either having been due to an increase of hydrogen in solution to the high stress region over that in the approximately unstressed section by the interaction energy factor, $\exp\left[\frac{p(gage)\cdot\bar{V}_H}{RT}\right]$ (their Eq. (1)) where $p(gage)$ is the hydrostatic stress increase from the bulk to the gage region, or the effect of stress on the solvus, which is given by the factor, $\exp\left[\frac{p(gage)\cdot(\bar{V}_H-\bar{V}_H^h)}{RT}\right]$. The experimental results show that, numerically, the deduced magnitude of the volume term is such that the increase must be given by the former expression since they were aware of the results of McEwen and co-workers [6] that show the two volumes in the latter expression being approximately equal in magnitude. In fact, as the solution to the Dutton–Puls model shows, when there is a stress gradient and hydrides can form, the correct answer is that given by the factor, $\exp\left[-\frac{p(gage)\cdot\bar{V}_H^h}{RT}\right]$. This result corresponds closely with that deduced from the experiments, both in terms of the correct magnitude for $\bar{V}_H^h$ and in the sign of the exponential. (Hydride formation occurs during cooldown in Kammenzind and co-workers' case with hydrogen in solution having increased according to the first term during the high temperature hold but, due to hysteresis, no hydride can precipitate at that temperature until a temperature is reached during cooldown at which the concentration in the gage section and in the bulk reaches TSSP. The net result of these two steps is that the contribution of the stress increase to hydrogen in solution given in the first expression cancels with the same term in the second, leaving the negative second part of the second exponential term as the proportionality factor for the increase in concentration in the gage region during each thermal cycle. This result is equivalent to the relative sink strength concentration at the crack tip in the steady-state diffusion equation solution of the Dutton–Puls model.)

The mechanism that Kim, however, proposes causing hydrogen redistribution under a stress gradient after cooling is curious. He says that "*Kammenzind's experiments have clearly demonstrated that a hydrogen transfer occurs only on cooling where the bulk volume shrinks hydrostatically.*" This statement seems to suggest that Kim believes the chemical potential for hydrogen in solution is: (i) affected by the decrease of the lattice spacing with decrease in temperature, whilst, (ii) at the crack tip, this effect of reduction in lattice parameter on the chemical potential is nullified by the high stresses there, which then causes hydrogen to migrate to the crack tip. Neither mechanistic nor direct experimental evidence is known to this author that could substantiate these beliefs.

Kim's claim for support of his criticisms of the original Dutton–Puls model also draws on words used in those early publications by Dutton and Puls that were correct given the data at that time, but which have now been superseded by new boundary conditions and data. Thus he points out that (the underlined part is a quote from the early papers [7,8]"*…they have never thought about precipitation or nucleation of the hydrides but just assume that all the hydrogen entering the crack tip region $r = \ell$ due to the hydrogen concentration gradient precipitates at the existing hydride…*". As mentioned in [2] and Appendix A, placing a hydride at the crack tip is done because the initial step of hydrogen diffusion to the crack tip to increase the hydrogen concentration there for hydride nucleation is neglected since the model only addresses the cases for which the solvus for hydride precipitation (nucleation) at the bulk would be exceeded as, otherwise, there would be no DHC. Therefore the author has clearly "*thought about*" hydride nucleation since it is built into the condition that a hydride is present at the crack tip, which could only occur if the concentration at the crack tip had increased to, or was already at, the solvus concentration for hydride nucleation. Specifically, in later versions of the model it is shown that the concentration of hydrogen in the bulk must be such that the stress gradient would be able to increase the hydrogen concentration at the crack tip so that it would meet or exceed the upper concentration range for hydride precipitation as determined, for instance, by Pan and co-workers [9]. These authors concluded that the upper concentration range of solvus data obtained for hydride precipitation, designated TSSP1, probably represents the solvus concentrations for hydride nucleation.

2.2. Comments on Section 2.2: Constant CGR independent of K_I

Kim claims that the Dutton–Puls model cannot predict the experimental observation that the crack growth rate is independent of K_I above $K_I > K_{IH}$. This is incorrect as shown by the author in [10] and additionally explained in [2,3]. Furthermore, McRae and co-workers [3], who give numerical predictions of the Dutton–Puls model by approximating the bulk stresses as being approximately zero whilst the crack tip stresses are limited by plasticity to some factor of the yield strength (and not K_I) – the latter being consistent with the boundary conditions in the original Dutton–Puls model – show that the model contains no dependence on K_I. Therefore Kim's statement that the model "*…cannot explain the constant Crack Growth Rate* (CGR) *independent of K_I…*" is only correct for the boundary conditions used in earlier numerical evaluations of the model. In these earlier evaluations all of the hydrogen flowing towards the crack tip from the bulk was chosen to come from the hydrogen in solution near hydrides in the bulk that would, on average, be closest to the crack tip hydride. However, in reality, hydrogen diffusing to the crack tip would come from all parts of the specimen, not just from a single, specific distance. Choosing a single, specific distance was done in the Dutton–Puls model to make the problem analytically tractable since the steady state solution requires the selection of such a specific distance from which there is a fixed concentration, independent of time, of hydrogen in solution. As there is no compelling physical reason for choosing what this distance should be, one could pick a distance very close to the crack tip hydride, where the concentration would be affected by K_I, as was done initially [7,8] or one could pick a distance far away, as was done in [3], where it would not depend on K_I.

Kim rejects the reasons given in the foregoing paragraph and also provided in [2], because, he claims, they are based on a faulty model. The author, however, has shown that the model is not faulty [2]. In particular, Kim states that the assertion of K_I independence should be numerically demonstrated, but rejects the example given in [2] taken from [10] (Fig. 1 reproduced in Kim's comments [1]) that demonstrate just this K_I independence. His reason for rejection the evidence presented in Fig. 1 of [10] is because that calculation – which is based on using theoretically determined elastic–plastic accommodation energies for the relevant solvi expressions in externally unstressed material – predicts too high a DHC arrest temperature. The fact that the numerical evaluation with these boundary solubilities results in too high a DHC arrest temperature compared to what is found experimentally does not invalidate the model's prediction of K_I independence. The K_I independence arises from the interaction energy term and not the accommodation energy terms governing the theoretical solvi, the latter being the reason for the predicted high arrest temperature.

Further, Kim rejects the author's claim in [2] that the model is capable of explaining the increase in crack growth rate with increase in yield strength. As pointed out, this dependence of the model on yield strength is due to the fact that the interaction energy term in the plastic zone of the crack, $\bar{w}^a_t(\ell)$, depends on the yield strength. Kim claims that in [2] no numerical evaluation of the model demonstrating this was given. This is only partially true as the results in [10], comparing DHC rate between unirradiated and irradiated material show how the model predicts the effect of changes in yield strength. However, this result was not specifically pointed out in [2]. There exists also another calculation that demonstrates the model's prediction of the effect of increase in yield strength on DHC rate which was made later by Sagat and co-workers [11], a reference that the author neglected to cite in [2].

2.3. Comments on Section 2.3: Effect of the direction approaching the test temperature on DHC

In this section Kim provides arguments as to why the author's claim that the Dutton–Puls model can explain the DHC arrest temperature when approached from below is incorrect. Again, the author is fixated on the earliest explanations for this arrest temperature which were based on the earliest and, moreover, highly speculative theoretical expressions for the solvi as applied by Ambler [12] when Kim should have referred to the most up-to-date analysis, which was that given in [13] in which the various arrest or initiation temperatures are evaluated on the basis of the Dutton–Puls model, but using experimentally determined solvi to calculate the bulk hydrogen concentration required to nucleate hydrides at the crack tip. As pointed out in [2], these calculations show fairly good agreement between predicted and measured arrest or initiation temperatures. Again, Kim's erroneous criticism is based on his overriding misconception that the various versions of the Dutton–Puls model are somehow fundamentally different, when as shown in the detailed derivations in Appendix A, they are simply different solutions due to the choice of more theoretically informed values for the solvus concentration at the crack tip and the hydrogen concentration in solution in the bulk, the latter of which is affected by hydrogen content and direction of approach to test temperature. Whether hydrides can nucleate or not is a key criterion in these analyses, in contradistinction to Kim's claim that this criterion is not part of the model. As evidence, Kim then cites the results of Resta Levi and Puls [14] to prove that this author cannot be correct. His claim is that this paper shows that crack arrest occurs despite metallographic evidence given in the paper showing that hydrides had repeatedly formed at the crack tip. However, the figure that Kim claims shows hydrides at crack arrest was in fact for a case in which DHC crack propagation was continually occurring (at a constant temperature just below the arrest temperature) and in which this process was deliberately stopped prior to total specimen failure to show the hydride distribution that had formed at the crack tip during progressive DHC steps.

2.4. Comments on Section 2.4: Crack tip concentrations

This section starts with a paragraph repeating Kim's erroneous understanding of the various DHC models. Again, the reader is referred to Appendix A for a systematic and detailed derivation of the various versions of the Dutton–Puls model showing that they all have the same thermodynamic basis contained in the original Dutton–Puls model, a point that is also made in [2], but not in such detail.

In the second paragraph Kim tries to prove that tensile stress at the crack tip does not increase the concentration of hydrogen there; in fact, he claims it decreases it there. It is clear, though, that he does not understand the meanings of the various hydrogen chemical potentials expressions derived by this author as demonstrated in the following.

Kim states that "*given the effect of tensile stresses that decreases the chemical potential of hydrogen as in [citing [2] as one of his references] [is]:*

$$\Delta\mu_H^{\sigma>0} = \Delta\mu_H^0 - \sigma \cdot V_H^h \qquad (1)$$

where $\Delta\mu_H^{\sigma>0}$ and $\Delta\mu_H^0$ are the chemical potential of hydrogen with and without tensile stresses, σ is the applied tensile stress, V_H^h is the increased volume due to precipitation of hydrides and $\sigma \cdot V_H^h$ corresponds to the so-called interaction energy, the stressed region should have a lower concentration than the unstressed region or the bulk. It occurs because the hydrogen solubility or hydrogen concentration in solution is determined by the chemical potential of hydrogen as shown in [Eq. (2)]:

$$\Delta\mu_H^0 = \mu_H^D - \mu_H^0 = RT\ell n C_H^D \qquad (2)$$

where μ_H^0 is the potential at the reference level, T temperature, C_H^D the diffusible hydrogen concentration. In other words, the applied stress has an effect on reducing the hydrogen solubility in the stressed region, causing the crack tip to have a lower hydrogen concentration in solution than the bulk, as shown in [Eq. (3)]:

$$C_H^D \text{at crack tip} < C_H^D \text{ in the bulk}'' \qquad (3)$$

Kim does not indicate how he arrives at the result in Eq. (3) with the use of Eqs. (1) and (2). The following is a guess. Substituting $\Delta\mu_H^0$ given by Eq. (2) into Eq. (1) yields:

$$\Delta\mu_H^{\sigma>0} = RT\ell n C_H^D - \sigma \cdot V_H^h \qquad (4)$$

It is then not clear how Kim would have used this Eq. (4) to arrive at his stated result. The only way would appear to be to set $\Delta\mu_H^{\sigma>0} = 0$. Then the concentration at the crack tip would be:

$$C_H^D = \exp\left[\frac{\sigma \cdot V_H^h}{RT}\right] \qquad (5)$$

However, this is a nonsensical result, since there is no pre-exponential concentration term. Moreover, the physical meaning of setting $\Delta\mu_H^{\sigma>0} = 0$ is also not clear. This is because the notation $\Delta\mu_H^{\sigma>0}$ implies that it is the difference between two chemical potentials, but between which states is not defined by Kim. Note also that the chemical potential of hydrogen in solution in the matrix at a hydride, which Kim gives as Eq. (6) (Eq. (1) in the foregoing) has a molar volume term missing, which is the molar volume of hydrogen in solution, denoted in [2] by V_H using Kim's notation. However, perhaps Kim means that V_H^h is the volume change (not the volume increase as stated) and therefore has a different meaning than that given by this author. This interpretation of the volume V_H^h would also not make sense since Kim has agreed that, numerically, $V_H \approx V_H^h$ and therefore the solvus is unaffected by stress. In addition, there is no stress-free solvus concentration indicated in Eq. (1). Finally, one might guess that Kim has erroneously constructed boundary hydrogen chemical potential expressions in Eqs. (1) and (2) that would correspond to the boundary concentration terms in the steady-state diffusion equation solution. These boundary concentration terms have, however, been shown to be relative sink strength values in the steady-state diffusion solution, combining the net effects of stress on hydrogen in solution and on the solvi. In summary, the correct derivation is given by this author in [2] and in Appendix A.

The final paragraph presents Kim's rebuttal of the author's claim that the Dutton–Puls model, when the thermo-mechanical history is such that the bulk concentration is given by TSSD, is capable of predicting that DHC would be possible at low temperatures up to some crack arrest temperature which is predicted to be not too different from those determined experimentally. The main point of this author was that the predictions of the model using the approach in [13], based on experimentally determined solvi values rather than theoretical estimates used in earlier treatments, and using slightly larger values for the plastic zone stresses, gave good agreement with the experimental results. Strangely, Kim cites [13] as supporting his claim that the model predicts (presumably at all temperatures) that DHC is not possible when the bulk hydrogen concentration corresponds to that for TSSD, in contradistinction to what was actually determined in [13] (see Fig. 7 in [13]).

3. Comments on Section 3: Kinetics of crack growth by DHC

Kim cites the TEM experiments of Cann and Sexton [15] as demonstrating that nucleation is the first step in DHC while the Dutton–Puls model says it is the diffusion of hydrogen to the crack tip. However the Cann and Sexton experiments show that hydrides did not form at the crack tip as soon as the sample was strained. The authors [15] note that "*…hydrides were generally detected within a few hours of the straining*". In addition, they mentioned that when a hydride fractured, a new one would not form until a few hours later. These observations all indicate that diffusion of hydrogen to the crack tip is the first step in DHC. Kim then argues that this author's assumption that the time for hydrogen diffusion to the crack tip is much less than the average hydride growth rate is unreasonable. This author agrees that this assumption is speculative, but it seems reasonable because the number of hydrogen atoms that need to arrive for the concentration at the crack tip to reach TSSP1 and for nucleation to commence would seem to be fewer, and hence this process would take less time, than the subsequent average growth of these hydride nuclei to combine to a critical size at the crack tip having dimensions of a few micrometer thick and many micrometers long.

Kim subsequently makes the statement that "*…given that the second phase particle of a higher molar volume can nucleate in metals with a lesser molar volume only under supersaturation conditions of solutes [28], nucleation of hydrides occurs only under hydrogen supersaturation or ΔC.*"

It is not clear what Kim means by supersaturation conditions as this requires a reference concentration from which this supersaturation is measured. In referring to the higher molar volume of the hydride with respect to the matrix, Kim presumably means the much higher hydride-matrix strain energy that is generated as a result of this increase in volume when a hydride nucleates as compared to the elastic–plastic accommodation energy required for subsequent hydride dissolution. This difference in the hydride-matrix accommodation energies between nucleation and dissolution has been proposed by this author to be the reason that the nucleation solvus is substantially higher in concentration compared to the dissolution solvus. Hence we guess that by supersaturation Kim means the difference in solvus concentration between that for nucleation (TSSP1) and that for hydride dissolution (TSSD). Now one of the ways this can be achieved in the Dutton–Puls model is by a stress-assisted diffusional increase of hydrogen, which Kim claims, erroneously, cannot be achieved at any temperature when the test temperature is approached from below according to this model. We have shown in Section 2.4 that this claim of Kim's is incorrect. Now, another way that the crack tip concentration can be increased to that of TSSP1 is in approaching the test temperature from above such that the hydrogen concentration everywhere in the specimen, including at the crack tip, would be at TSSP1. Kim claims that this is the only way that DHC can be predicted with the Dutton–Puls model, but this author's examples in [2] and in Appendix A, show that Kim is incorrect in this assertion. In addition, approaching the test temperature from above with the specimen everywhere at TSSP1 is not really a supersaturation condition from the point of view of DHC, since the concentration required at the crack tip is also that at TSSP1. One might more accurately say that when TSSD determines the bulk hydrogen concentration, or when the concentration is anywhere in between this value and that of TSSP1, it is undersaturated with respect to nucleation of hydrides at the crack tip and requires some tensile-stress-assisted diffusional increase there to remove this undersaturation.

The final part of Kim's rebuttal in this section concerns this author's assertion that the mechanism of stress-assisted δ hydride formation at the crack tip proposed by Kim as an important mechanism enabling low temperature DHC is not credible. Kim's main rebuttal in this section concerns confirming the experimental evidence that, in his view, points to the γ hydride phase being the stable phase in the bulk below 180 °C (higher for water-quenched specimens) while it is the δ hydride phase that precipitates at the crack tip during DHC. However, Kim did not address the question posed by this author of why the δ hydride phase should form at the crack tip under these circumstances, when the γ hydride phase is claimed, or shown, to be the stable phase in the bulk. Kim simply states that "*Below 180 °C, however, the supersaturation of hydrogen* [between crack tip and bulk] *is created due to stress induced hydride phase transformation from γ to δ where the γ-hydride has a higher solubility than the δ-hydride.*" The question posed by this author [2] was, what is the mechanism for this stress-induced phase transformation from γ to δ at the crack tip and why would the solvus at the crack tip be lowered to exactly the magnitude of TSSD for these δ hydrides when, experimentally, it is shown that hydride nucleation and growth is governed by TSSP (both in magnitude and direction (i.e. precipitation rather than dissolution of hydrides))? To this author's knowledge, no such mechanism exists, which is presumably why Kim has merely stated that such a mechanism exists without actually showing what thermodynamic relations would be driving such a solvus conversion. Without Kim supplying a credible answer to this question, it is irrelevant whether or not the γ hydride phase in the bulk is stable and whether or not it has a higher TSSD than the δ hydride phase. Also, the claim that TSSD of the δ hydride phase has a lower concentration than that of the γ hydride phase at these low temperatures would seem to rest on the validity of extrapolating fits of TSSD data obtained from measurements above 150 °C to the lower temperature range plus making the argument that the very few TSSD data below this temperature, of higher concentration than the corresponding extrapolated TSSD values, represent the solubility of the γ hydride phase. (Actually, some of the supporting references that Kim cites for this do not show a difference in slope and, hence, higher values at lower temperatures, for the TSSD data, only for the TSSP data [16,17].) In addition Kim suggests that this extrapolated value of TSSD for the δ hydride phase then applies to a stress-stabilized δ hydride phase that would form preferentially at the crack tip in favour of the stable γ hydride phase that governs the solvus in the bulk. In addition, since it is TSSP1 that is actually required at the crack tip for hydrides to form in terms of direction of the phase transformation, this precipitation solvus has somehow been reduced in magnitude there to be equivalent to that of TSSD for the δ hydride phase, again, due to some stress-assisted mechanism. This is a highly speculative and convoluted argument for an explanation of a result that this author has shown can be readily demonstrated with the Dutton–Puls model [13] on the basis of a much more straight-forward and credible physical mechanism.

4. Conclusions

The author has shown in this rebuttal that Kim has failed to provide any new arguments to support his claim that the Dutton–Puls model for DHC rate is based on a faulty thermodynamic basis and is incapable of correctly predicting some key experimental findings. Thus, the author feels that the previous criticisms of Kim's model as well as the author's defense of the correctness of the thermodynamic basis of the various versions of the Dutton–Puls models [2] have been validated. In contradistinction, the author shows in this and the initial criticism [2] that it is Kim's DHC model that has a faulty thermodynamic basis and, therefore, is not viable in underpinning our understanding of DHC rate.

Appendix A. Detailed derivations of the diffusion equation solutions of the Dutton–Puls model

A.1. Detailed derivation of the original Dutton–Puls model

The following derivation differs from that given originally by Dutton and Puls [7,8] in using the more commonly used convention of tensile stresses being positive. In addition, only the first order work term is retained in the expression for the chemical potential. The notation used in this appendix follows that used in [2] and differs from that used in the main body of this article, which follows the notation used by the authors.

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

$$\mu_H^D(r,p) = \mu_H^o + RT\ell n c_H^D(r,p) - p(r)\cdot\bar{V}_H \tag{A1}$$

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 meanings. The variation of $c_H^D(r,p)$ with stress is obtained by noting that, at zero stress from Eq. (A1), we have

$$\mu_H^D(r,0) = \mu_H^o + RT\ell n c_H^D(r,0) \tag{A2}$$

Equilibrium between the regions at zero and at non-zero stresses is obtained when the chemical potentials for diffusion given by Eqs. (A1) and (A2) are equal. This yields that the concentration in the stressed part of the crystal is increased over that in the unstressed part according to

$$c_H^D(r,p) = c_H^D(r,0)\cdot\exp[p(r)\cdot\bar{V}_H/RT] \tag{A3}$$

When hydrides are present in the unstressed region, we obtain from Eq. (A3):

$$c_H^{D,o}(r,p) = c_H^s(r,0)\cdot\exp[p(r)\cdot\bar{V}_H/RT] \tag{A4}$$

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 and, therefore, is identified with the superscript 'o' to identify it as such.

When the hydrogen concentration in the alpha phase has reached its terminal (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:

$$\mu_H^B(r,p) = \mu_H^o + RT\ell n c_H^B(r,p) - p(r)\cdot\bar{V}_H + p(r)\cdot\bar{V}_H^h \tag{A5}$$

Local equilibrium is achieved when the chemical potential for diffusion, given by Eq. (A1) is equal to the boundary chemical potential given by Eq. (A5). Equating these chemical potentials and choosing as the reference concentration for $c_H^D(r,p)$ the value given by Eq. (A4), yields:

$$\begin{aligned}&\mu_H^o + RT\ell n c_H^B(r,p) - p(r)\cdot\bar{V}_H + p(r)\bar{V}_H^h\\ &\quad = \mu_H^o + RT\ell n c_H^{D,o}(r,p) - p(r)\cdot\bar{V}_H\end{aligned} \tag{A6}$$

which, after some algebra, yields the following boundary (solvus) concentration at a specified location, r:

$$\begin{aligned}c_H^D(r,p) &= c_H^B(r,p)\\ &= c_H^s(r,0)\cdot\exp[-p(r)\cdot\bar{V}_H^h/RT]\exp[p(r)\cdot\bar{V}_H/RT]\end{aligned} \tag{A7}$$

where $c_H^s(r,0)$ is the solvus concentration at zero external stress at r. Eq. (A7) shows how external stress affects the solvus, $c_H^s(r,0)$, that is measured under zero external stress. Note then that if $\bar{V}_H^h = \bar{V}_H$, this equation predicts that external stress has no affect on the hydrogen solvus concentration.

The diffusion flux of hydrogen, J_H, is

$$J_H = -\frac{c_H^*)\cdot D_H}{RT}\nabla\mu_H^D(r,p) \equiv -\frac{c_H^D(r,p)\cdot D_H}{\Omega_{Zr}\cdot RT}\nabla\mu_H^D(r,p) \tag{A8}$$

and using Eq. (A1) assuming the problem is cylindrically symmetric, this relation becomes

$$J_H = -\frac{D_H}{\Omega_{Zr}}\left\{\frac{dc_H^D(r,p)}{dr} - \frac{\bar{V}_H\cdot c_H^D(r,p)}{RT}\frac{dp(r)}{dr}\right\} \tag{A9}$$

In Eqs. (A8) and (A9): $c_H^*(r,p)$ is the number of hydrogen atoms/unit volume, $c_H^D(r,p)$ 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, $\mu_H^D(r,p)$ the chemical potential for diffusion given by Eq. (A1), $\bar{V}_H$ is the molar volume of hydrogen in α-Zr.

At steady state

$$\nabla\cdot J_H = 0 \tag{A10}$$

Carrying out this divergence operation, with J_H given by Eq. (A9) yields

$$\frac{1}{r}\frac{d}{dr}\left\{rD_H\left(\frac{dc_H^D(r,p)}{dr} - \frac{\bar{V}_H\cdot c_H^D(r,p)}{RT}\frac{dp(r)}{dr}\right)\right\} = 0 \tag{A11}$$

Integrating Eq. (A11) once, yields

$$\frac{dc_H^D(r,p)}{dr} - \frac{\bar{V}_H\cdot c_H^D(r,p)}{RT}\frac{dp(r)}{dr} = -\frac{K_1}{r} \tag{A12}$$

Making a change in variable in Eq. (A12) as follows:

$$c_H^D(r,p) = c_H^{D*}(r,p)\cdot\exp\left(\frac{p(r)\cdot\bar{V}_H}{RT}\right) \tag{A13}$$

and integrating the resultant expression, yields

$$c_H^{D*}(r,p) = -K_1 \int \frac{dr}{r} \exp\left[\frac{p(r)\cdot \bar{V}_H}{RT}\right] + K_2 \tag{A14}$$

which, changing back to the original variable using Eq. (A13), becomes

$$c_H^{D}(r,p) \exp\left[-\frac{p(r)\cdot \bar{V}_H}{RT}\right] = -K_1 I(r) + K_2 \tag{A15}$$

with

$$I(r) = \int \frac{dr}{r} \exp\left[\frac{p(r)\cdot \bar{V}_H}{RT}\right] \tag{A16}$$

Since the left hand side of Eq. (A12) is equal to the quantity in the curly brackets of Eq. (A9), then the flux, J_H, is given by

$$J_H = -\frac{D_H}{\Omega_{Zr}}\left[-\frac{K_1}{r}\right] \tag{A17}$$

Hence, we need only solve for the constant, K_1, to get the steady state solution for the diffusion equation. The boundary conditions are as follows:

At $r = \ell$

$$c_H^D(\ell,p)\exp[-p(\ell)\cdot \bar{V}_H/RT] = c_H^s(\ell,0)\cdot \exp[-p(\ell)\cdot \bar{V}_H^h/RT] \tag{A18}$$

whilst at $r = L$

$$c_H^D(L,p)\exp[-p(L)\cdot \bar{V}_H/RT] = c_H^s(L,0)\cdot \exp[-p(L)\cdot \bar{V}_H^h/RT] \tag{A19}$$

These two conditions implicitly imply that the hydrogen content in the material is such that hydrides would be able to form at the crack tip and would be present in the bulk, respectively. The constant, K_1, is obtained by inserting these boundary conditions into Eq. (A15), yielding the following equations:

$$c_H^s(\ell,0)\cdot \exp[-p(\ell)\cdot \bar{V}_H^h/RT] = -K_1 I(\ell) + K_2 \tag{A20}$$

$$c_H^s(L,0)\cdot \exp[-p(L)\cdot \bar{V}_H^h/RT] = -K_1 I(L) + K_2 \tag{A21}$$

Subtracting Eq. (A20) from Eq. (A21), eliminates K_2 and yields an equation for K_1:

$$\begin{aligned} &c_H^s(L,0)\cdot \exp\left[-\frac{p(L)\bar{V}_H^h}{RT}\right] - c_H^s(\ell,0)\cdot \exp\left[-\frac{p(\ell)\bar{V}_H^h}{RT}\right] \\ &\quad = K_1\cdot [I(L) - I(\ell)] \end{aligned} \tag{A22}$$

with

$$I(L) - I(\ell) \equiv I(\ell,L) = \int_\ell^L \left(\frac{dr}{r}\exp\left[\frac{p(r)\cdot \bar{V}_H}{RT}\right]\right) \tag{A23}$$

Inserting the value for K_1 given by Eq. (A22) into Eq. (A15) yields

$$J_H = -\frac{D_H}{\Omega_{Zr}\cdot I(\ell,L)\cdot r}\left[c_H^s(L,0)\cdot \exp\left[-\frac{p(L)\bar{V}_H^h}{RT}\right] - c_H^s(\ell,0)\cdot \exp\left[-\frac{p(\ell)\bar{V}_H^h}{RT}\right]\right] \tag{A24}$$

Eq. (A24) can be written

$$J_H = -\frac{D_H\cdot \exp\left[-\frac{p(L)\cdot \bar{V}_H^h}{RT}\right]}{\Omega_{Zr}\cdot I(\ell,L)\cdot r}\left[c_H^s(L,0) - c_H^s(\ell,0)\cdot \exp\left[-\frac{\Delta p(\ell,L)\cdot \bar{V}_H^h}{RT}\right]\right] \tag{A24$'$}$$

with $\Delta p(\ell,L) = p(\ell) - p(L)$. Eq. (A24), or Eq. (A24′), then, is the solution for the steady-state diffusion flux of hydrogen to the crack tip with the latter being identical to the result given by Eq. (13) in [7], or Eq. (8) in [8] except for the difference in sign in the exponential terms that arises out of the difference in sign convention for tensile stresses between this and the other two references. Note that the concentrations in the square brackets are not the solvi concentrations at $r = L$ and ℓ, respectively. These are given by Eq. (A5) when $r = \ell$ or L and show that the solvi are unaffected by external stress when $\bar{V}_H^h = \bar{V}_H$. The concentrations in the square bracket in Eq. (A24) are actually effective concentrations giving the relative sink strengths of the hydrides at $r = \ell$ and L, respectively, and take this stress-dependence as a consequence of the contribution of the stress gradient driving hydrogen from regions of lower to regions of higher tensile stresses, which is factored into the solution for this equation.

A.2. First modification to the original Dutton–Puls model

Evidence that the solvus measured in heat-up experiments was substantially different from that in cool-down experiment; i.e., that there is a large hysteresis between the two, led this author to make various attempts at developing a theoretical model to explain this phenomenon [10,19–21]. The first of these attempts drew its inspiration from earlier and parallel theoretical considerations proposed by Paton et al. [22] and Birnbaum and co-workers [23,24], respectively. The basic premise in the earliest of these solvi models was that hydrides, on first forming in the alpha zirconium matrix, are elastically constrained. The constraint arises because hydrides have a positive strain misfit with the alpha zirconium matrix from which they have transformed and because they are assumed to have a coherent interface with the surrounding matrix as a result of them being very small and incapable of relieving their large misfit strains by plastic deformation. The resultant maximum strain energies of the material when a hydride of a specified shape and misfit strains forms were calculated using the methods and insights developed by Eshelby [25]. To explain the hysteresis between heat-up and cool-down solvi that was found experimentally it was further assumed – erroneously, in the first attempt, in terms of the estimated magnitude – that this theoretical, maximum elastic strain energy would all be converted during hydride growth and then lost on phase reversal by the production of a similar magnitude of plastic work.

The development of this model for TSS also led to an improved version for the $-p(r)\cdot \bar{V}_H^h$ component of the interaction energy. The improved version takes proper account of the fact that when hydrogen transfers from the matrix to the hydride, the work done must be that due to the strain misfit produced by the formation of the hydride phase in its entirety – taking proper account of its orientation – rather than the simple transfer of a molar volume of hydrogen in solution to that in the hydride. Further details of these derivations and the theoretical bases that support them are given in [19].

A crucial feature of the model for the solvus was that the shifts in the solvi concentrations due to elastic constraints and plastic work are calculated with respect to what is referred to as a stress-free solvus, $c_H^s(r,0)$, which is the solvus for incoherent equilibrium. It was assumed at the time that the isothermal dissolution experiments of Kearns [26] provided such a value. This belief turned out to be incorrect, although the magnitude of the difference between the correct value and Kearns' result was later calculated to be relatively small, but not insignificant.

The modified equation for the fully constrained solvus results in a modified boundary hydrogen concentration expression, $c_H^B(r,p)$, given by:

$$\begin{aligned} c_H^B(r,p) = c_H^s(r,0)\cdot \exp\left[\frac{\bar{w}_t^{inc}(r)}{RT}\right]\exp\left[\frac{\bar{w}_t^{a}(r)}{RT}\right] \\ \cdot \exp\left[\frac{p(r)\cdot \bar{V}_H}{RT}\right] \end{aligned} \tag{A25}$$

where[1]

$$\bar{w}_t^a(r) = -\frac{\bar{V}_{Zr}}{x}\cdot \sigma_{ij}(r)\cdot e_{ij}^T \tag{A26}$$

and $\bar{V}_{Zr}$ = partial molar volume of zirconium, σ_{ij} = applied stresses (positive if tensile), e_{ij}^T = stress-free transformation strains to

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[1] As discussed in [2], all previous publications erroneously used $\bar{V}_{hydride}$ instead of $\bar{V}_{Zr}$ in Eq. (A26).

transform α-Zr to zirconium hydride, x = composition of hydride phase (ZrH_x), $\bar{w}_t^{inc}(r)$ = total molar elastic strain energy of hydride (inclusion) and matrix and with the interaction energy term, $\bar{w}_t^a$, replacing the term previously given by $-p(r) \cdot \bar{V}_H^h$. As pointed out in [2], there is little numerical difference between $-p(r) \cdot \bar{V}_H^h$ and $\bar{w}_t^a(r)$.

Utilization of the boundary conditions given by Eqs. (A25) and (A26) at $r = \ell$ and L, yields for the steady-state diffusion flux

$$J_H = -\frac{D_H \cdot c_H^s(0)}{\Omega_{Zr} \cdot I(\ell, L) \cdot r}\left[\exp\left[\frac{\bar{w}_t^{inc}(L)}{RT}\right]\exp\left[\frac{\bar{w}_t^a(L)}{RT}\right] - \exp\left[\frac{\bar{w}_t^{inc}(\ell)}{RT}\right]\exp\left[\frac{\bar{w}_t^a(\ell)}{RT}\right]\right] \tag{A27}$$

Eq. (A27) is the diffusion flux part of the DHC velocity expression in Eq. (3) of [18][2]. Examples of the use of this equation to rationalize the TSS and DHC velocity data at the time are given in [18–21]. Note that the only change in the model at that time was an improved representation of the boundary solvi concentrations. Strictly speaking, this revised model, as with the original one, is valid only when hydrides are present in the bulk (L) and can act as sources of hydrogen in solution, thus serving to keep the hydrogen concentration in solution at L at a fixed value, which is what is needed for steady-state conditions to be strictly applicable.

A.3. Second modification to the Dutton–Puls model

In subsequent versions further changes in the diffusion flux equation again involved only changes to the formulation of the solvus/boundary concentrations. These changes arose out of improved insights into the mechanistic origins of the hysteresis in the solvi. The improved understanding resulted in different numerical values for the boundary concentrations given by Eqs. (A25), (A26), depending on the assumed values for the accommodation energy, with this energy taken on a more complex, generalized form that might or might not include plastic work terms, depending on the thermal history of the material prior to arriving at the test temperature. In particular, it was assumed that DHC initiation and continued propagation requires that the concentration at the crack tip must be sufficient for hydride nucleation. It was conjectured that the experimentally determined crack tip solvus denoted as TSSP1 by Pan and co-workers [9] was the appropriate solvus for hydride nucleation. Theoretically this solvus concentration is given by $c_H^s(r, 0) \cdot \exp\left[\frac{\bar{w}_t^{inc}(r)}{RT}\right]$ where $\bar{w}_t^{inc}(r)$ is the total molar elastic strain energy of hydride and matrix. Numerical evaluation of this term and of $\bar{w}_t^a(r)$ at a crack tip had already shown that these two terms were closely similar in magnitude [19], but opposite in sign, which means that the concentration given by the second term in Eq. (A27) is approximately equal to $c_H^s(0)$. This provided justification, it seems, for Kim to assert that the solvus at the crack tip is equal to TSSD, since he made the erroneous conclusion that the concentrations in the square bracket of Eq. (A27) are the solvi concentrations at $r = \ell$ and L, whilst, in fact, the stress-affected solvi concentrations are those given by Eqs. (A25) and (A26). Moreover, $c_H^s(0)$ is also not exactly equal to TSSD. It must be derived from experimental TSS values, all of which are shifted from the stress-free or chemical solvus due to elastic–plastic accommodation energy contributions, the determination of which requires theoretical calculations. Available results indicate, though, that the difference between TSSD and $c_H^s(0)$ is not large (although not insignificant), being smaller than the hysteresis between TSSD and TSSP [27], so Kim is approximately correct that $c_H^s(0) \approx c_H^s(TSSD,\ stress\ free)$, but $c_H^s(0)$ is not, by its definition, the solvus in an externally stressed crystal. The solvus in an externally stressed material is given by Eqs. (A25) and (A26), which becomes at the crack tip, assuming, numerically, that $c_H^s(0) \approx c_H^s(TSSD,\ stress\ free)$ and $\bar{w}_t^{inc}(\ell) \approx \bar{w}_t^a(\ell)$,

$$c_H^B(\ell, p) \equiv c_H^{B,s}(\ell, p) \approx c_H^s(TSSD,\ stress\ free) \cdot \exp\left[\frac{p(\ell) \cdot \bar{V}_H}{RT}\right] \tag{A28}$$

Eq. (A28) shows that the solvus concentration subjected to the stresses existing at the crack tip is approximately equal to the solvus for TSSD under zero stress times the factor, $\exp\left[\frac{p(\ell) \cdot \bar{V}_H}{RT}\right]$. However, this factor is just the increase in hydrogen concentration at the crack tip that is produced by the stress gradient term in the diffusion equation, which is embodied in the solution given by Eq. (A27) and therefore in terms of the bulk concentration of hydrogen in solution, it appears as though the limit for hydride precipitation at the crack tip occurs approximately at the TSSD concentration determined in externally unstressed material. It is worth emphasizing that this effective reduction is only approximately equal to TSSD as the work term, $\bar{w}_t^a(r)$, and the strain energy, $\bar{w}_t^{inc}$, are two different physical quantities, the first involving the yield strength, the second only elastic constants at this level of approximation, and with both depending on the misfit strains, but, again, in different ways. Therefore, near numerical equality of the absolute values of these two parameters may not necessarily apply to the complete range of temperatures and crack tip stress state conditions. Moreover, this prediction is a theoretical one and is speculative in terms of whether it is quantitatively correct in its description of TSSP and the hydride interaction energy at the crack tip.

Because of the speculative nature of the theoretical interpretation of the experimentally determined TSS values, the most straight-forward final formulation of the boundary concentrations would be in terms of the experimentally determined solvi measured in externally unstressed material. In moving towards this approach in subsequent studies, in a numerical assessment of the steady state solution of the Dutton–Puls model by this author [10], the boundary value concentrations were re-formulated to more general expressions that could be applied either using theoretically predicted solvi concentrations or measured ones obtained under zero external stress. In the assessment by this author in [10], theoretical values were used, but based on analytical solutions of purely elastic and elastic plastic accommodation energies. Unfortunately a drawback to this approach at the time was that the analytically determined elastic–plastic accommodation energies were for spherically-shaped hydrides only, the values of which were found from later finite element calculations to have significantly different accommodation energies compared to plate-shaped morphologies that more realistically represent the shapes of hydrides formed in the bulk and at the crack tip.

The boundary condition that applied to precipitation at the crack tip naturally was that given by TSSP which was denoted by c_H^{cool} [10]. To be consistent with the present notation this solvus concentration will be denoted by $c_H^{s,cool}(0)$ the zero inside the brackets emphasizing that it is the experimentally determined solvus for hydride precipitation in externally unstressed material. The concentration is given the superscript '*cool*' in recognition of the fact that most of the data for this solvus was determined experimentally under cool-down conditions. The boundary solvus concentration at the crack tip at $r = \ell$ is then

$$c_H^B(\ell, p) = c_H^{s,cool}(0) \cdot \exp\left[\frac{\bar{w}_t^a(\ell)}{RT}\right] \cdot \exp\left[\frac{p(\ell) \cdot \bar{V}_H}{RT}\right] \tag{A29}$$

In anticipation of reformulating the diffusion equation solution in a simpler algebraic form, Eq. (A29) was then rewritten as

$$c_H^B(\ell, p) = E_\ell \cdot \exp\left[\frac{p(\ell) \cdot \bar{V}_H}{RT}\right] \tag{A30}$$

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[2] Note that the sign of that equation in [18] is incorrect.

with

$$E_\ell = c_H^{s,cool}(0) \cdot \exp\left[\frac{\bar{w}_t^a(\ell)}{RT}\right] \tag{A31}$$

Since experimentally it is found that TSSP can have a range of possible values, there remains the uncertainty as to which of the possible range of measured TSSP values applies to DHC.

Regarding the concentration in the bulk, at $r = L$, it was recognized already by Simpson and Puls [18] that what mattered regarding whether DHC could occur or not and what the rate would be was the concentration of hydrogen in solution and not whether hydrides are present or not in the bulk. In the original Dutton–Puls model it was assumed that hydrides must be present in the bulk because that is what the early results appeared to show, but also because it assured the constancy of the hydrogen concentration at $r = L$ when hydrides are present, since these hydrides can act as a large reservoir of hydrogen to replenish the hydrogen in solution that would continually flow to the crack tip. This then assured the validity of the steady state assumption that led to the solution of the diffusion flux, Eq. (A24). However, as the authors have indicated, it is probably not a bad approximation to assume that there would be little change in the bulk hydrogen concentration in solution even when it is not being replenished by dissolution of hydrides there. Hence, the concentration in the bulk, at $r = L$, could have different values depending on the previous thermal–mechanical history of the material leading up to the test temperature conditions. There are three possibilities. The first is that the hydrogen in solution is determined by TSSD which corresponds to the case given in the original Dutton–Puls model. From Eq. (A24), the boundary concentration in solution at $r = L$, re-formulated in the same way as given by Eqs. (A30) and (A31), is then given by:

$$c_H^B(L,p) = c_H^{s,heat}(0) \cdot \exp\left[\frac{\bar{w}_t^a(L)}{RT}\right] \cdot \exp\left[\frac{p(L) \cdot \bar{V}_H}{RT}\right] \tag{A32}$$

Eq. (A29) is rewritten as

$$c_H^B(L,p) = E_L \cdot \exp\left[\frac{p(L) \cdot \bar{V}_H}{RT}\right] \tag{A33}$$

with

$$E_L = c_H^{s,heat}(0) \cdot \exp\left[\frac{\bar{w}_t^a(L)}{RT}\right] \tag{A34}$$

The second possibility is that the test temperature is approached from above and the hydrogen content in the material is such that the concentration in the bulk follows TSSP. In that case, Eqs. (A32) and (A34) are modified by replacing $c_H^{s,heat}(0)$ with $c_H^{s,cool}(0)$. In this example the hydrogen concentration in solution would not be replenished by dissolution of the hydrides present in the bulk until the concentration at that location would be reduced to a level corresponding to that given by TSSD at that temperature. Note that approaching the temperature from above now makes DHC possible at temperatures at which it would not be possible when TSSD determined the hydrogen concentration at L, since the hydrogen in solution is now greater.

The third case concerns a thermal–mechanical history and a hydrogen content for which $c_H^{s,heat}(0)$ would be given by the total hydrogen content in the sample, c_H^0. If this case were to apply there would, of course, be no hydrides present in the bulk and eventually a test temperature would also be reached, as the test temperature is increased, at which DHC would cease to be possible due to insufficient bulk hydrogen concentration in solution for hydride precipitation at the crack tip or due to hydrides not being able to fracture even though they had formed.

The steady state solution of the diffusion flux equation, with the notation for the boundary concentrations at ℓ and at L as given by Eqs. (A29)–(A34), is now given by:

$$J_H = -\frac{D_H}{\Omega_{Zr} \cdot I(\ell, L) \cdot r}[E_L - E_\ell] \tag{A35}$$

A.4. Third modification of the Dutton–Puls model

In a final modification of the Dutton–Puls model, the time-dependence of the diffusion flux was explored by not assuming that steady-state conditions prevailed [28,29]. This modification made it possible to calculate the growth rate of hydride formed at the crack but at the cost of not having a closed-form analytic solution for this growth rate. An added departure from the original Dutton–Puls solution was the assumption that the thickness of the hydride plate at the crack remains constant during hydride growth. Other assumptions made in the original Dutton–Puls model were, however, retained such as

(a) the crack tip stresses were assumed to depend only on the cylindrical coordinate, r;
(b) the hydrogen diffusion field is isotropic;
(c) all hydrogen entering into the circular radius centered at the crack (hydride) front collapses into a plate- or cylindrically-shaped hydride precipitate.

For the boundary condition at the crack tip to determine whether hydrides could form or not, advantage was taken of the fact that theory had shown that the effect of stress on the solvus (TSS) was sufficiently small that it could be neglected. Therefore this model is essentially the same as the original Dutton–Puls model except for eliminating the stress-dependence of the solvi concentrations.

Given the foregoing assumptions, the diffusion equation has the same form as in Eq. (A9). However, the time-dependence of the diffusion flux and, hence, the corresponding time-dependence of the growth of the hydride plate was evaluated using a diffusion solution solver with time-dependent, moving boundaries. The boundary condition at the hydride – once it was shown that the diffusion solution elevated the hydrogen concentration sufficiently for hydride to form at the crack tip – was the stress-unaffected precipitation solvus, TSSP. The hydrogen concentration in the bulk could, in general, have a starting concentration given by the three possible values given in Section 3. For the details of the results of these calculations the reader is referred to the relevant references [28,29].

The foregoing model was then also used to derive expressions for the various DHC limit temperatures [13]. Although, for simplicity, the potential stress-dependences of the solvi were not included in these derivations, they could have been easily included, but this inclusion would have had little numerical impact on the final results as shown in the following example where the results for the two approaches are compared. In both examples the bulk hydrogen concentration at which DHC is possible is derived for the case when the test temperature is approached from a peak temperature at which all hydrides had been dissolved.

The first derivation is that by Shi et al. [13] where it is assumed that the solvus at the crack is unaffected by stress and this is followed with the derivation for a similar relationship obtained by Puls et al. [27] where it is assumed that the solvus could be affected by stress. In both derivations, the maximum hydrogen concentration, $c_H^{\max}$, at the crack tip due to stress-affected diffusion is

$$c_H^{\max} = \beta \cdot c_H^0, \tag{A36}$$

with,

$$\beta = \frac{\exp\left[\frac{[p(\ell)-p(L)]\cdot\bar{V}_H}{RT}\right]}{1+\frac{1}{3}\cdot\frac{p(L)\cdot\bar{V}_H}{RT}} \approx \exp\left[\frac{p(\ell)\cdot\bar{V}_H}{RT}\right] \textit{when}\ \mathrm{L}\to\infty \tag{A37}$$

where c_H^0 is the bulk hydrogen concentration in solution in the material, ℓ the distance from the flaw tip to the maximum hydrostatic stress on the crack plane, and L is the effective diffusion distance.

Now, denoting c_H^0 as $c_H^{bulk}(DHC)$, then we have, when the stress effect is ignored

$$c_H^{\max} = c_H^{s,cool} \equiv c_H^s(TSSP1) \tag{A38}$$

or, when it is included in the solvus,

$$c_H^{\max} = c_H^{s,cool} \equiv c_H^s(TSSP1)\cdot\exp\left[\frac{\bar{w}_t^a}{RT}\right]\cdot\exp\left[\frac{p(\ell)\cdot\bar{V}_H}{RT}\right] \tag{A39}$$

Eq. (A38) could also be written in the original Dutton–Puls formulation, using $-p(\ell)\cdot\bar{V}_H^h$ rather than $\bar{w}_t^a$, giving

$$c_H^{\max} = c_H^{s,cool} \equiv c_H^s(TSSP1)\cdot\exp\left[-\frac{p(\ell)\cdot\bar{V}_H^h}{RT}\right]\cdot\exp\left[\frac{p(\ell)\cdot\bar{V}_H}{RT}\right] \tag{A40}$$

Now in the derivation by Shi and co-workers [14], in which the stress-dependence of the solvus is ignored, from Eqs. (A36), (A37) and using Eq. (A38) for $c_H^{\max}$, the bulk concentration for DHC, $c_H^{bulk}(DHC)$, is given by

$$c_H^{bulk}(DHC) = c_H^s(TSSP1)\cdot\exp\left[-\frac{p(\ell)\cdot\bar{V}_H}{RT}\right] \tag{A41}$$

whilst in the Puls and co-workers' [28] derivation where the stress-dependence is formally included $c_H^{bulk}(DHC)$ is given by

$$c_H^{bulk}(DHC) = c_H^s(TSSP1)\cdot\exp\left[\frac{\bar{w}_t^a}{RT}\right] \tag{A42}$$

when using Eq. (A39) for the effect of stress on the solvus, or

$$c_H^{bulk}(DHC) = c_H^s(TSSP1)\cdot\exp\left[-\frac{p(\ell)\cdot\bar{V}_H^h}{RT}\right] \tag{A43}$$

when using Eq. (A40) for the effect of stress on the solvus.

Eqs. (A41), (A42), (A43) all give numerically similar results for the bulk concentration at which DHC starts, but that given by Eq. (A42) is the physically more accurate expression. All three expressions show that hydride precipitation (and hence DHC) can initiate at bulk concentrations that are lower than those required for hydrides to precipitate in the bulk.

It is seen that the derivations for the various permutations of the solution of the hydrogen diffusion equations follow straightforwardly from the original model simply by making the appropriate modifications to the boundary value hydrogen concentrations. This demonstrates that the original Dutton–Puls model provides the thermodynamic basis for all subsequent models. In the following Section A.5, the solution to Kim's diffusion equation, which does not contain the stress gradient term, is derived and the result contrasted and compared with those obtained with the Dutton–Puls model given in Sections A.1–A.4.

A.5. Kim's diffusion equation solution

According to Kim there is no hydrogen diffusion flux to the crack tip due to the stress gradient. Thus his diffusion equation is that of Eq. (A9) with the stress gradient term removed:

$$J_H = -\frac{D_H}{\Omega_{Zr}}\frac{dc_H^D(r,p)}{dr} \tag{A44}$$

At steady state, the divergence of J_H is zero, which yields, in cylindrical coordinates:

$$\frac{1}{r}\frac{d}{dr}\left\{rD_H\frac{dc_H^D(r,p)}{dr}\right\} = 0 \tag{A45}$$

Integrating this equation yields

$$\frac{dc_H^D(r,p)}{dr} = -\frac{K_1}{r} \tag{A46}$$

which, when inserted into Eq. (A44) yields

$$J_H = -\frac{D_H}{\Omega_{Zr}}\left(-\frac{K_1}{r}\right) \tag{A47}$$

The constant, K_1, is obtained from integrating Eq. (A46) and the boundary conditions at $r = \ell$ and L yielding:

$$c_H^B(\ell,p) = -K_1\cdot\ell n\,\ell + K_2 \tag{A48}$$

$$c_H^B(L,p) = -K_1\cdot\ell n\,L + K_2 \tag{A49}$$

which results in

$$K_1 = -\frac{c_H^B(L,p)-c_H^B(\ell,p)}{I(\ell,L)} \tag{A50}$$

with

$$I(\ell,L) = \ell n\frac{L}{\ell} \tag{A51}$$

Thus the steady-state diffusion solution is

$$J_H = -\frac{D_H}{\Omega_{Zr}\cdot r\cdot I(\ell,L)}\left(c_H^B(L,p)-c_H^B(\ell,p)\right) \tag{A52}$$

In the case where the boundary concentration in the bulk at $r = L$, is given by $c_H^B(L,p) = c_H^s(TSSP)$, it must be that $c_H^B(\ell,p) < c_H^s(TSSP)$ for hydrides to form at the crack tip. However, we have seen that TSS is approximately unaffected by stress, so at $r = \ell$ it is approximately equal to $c_H^s(TSSP1)$, which is the experimentally determined solvus for hydride nucleation. Hence, with these choices of boundary concentrations, no hydrogen would flow towards the crack tip since the solvus at the crack tip is greater than or equal to the solvus in the bulk. Thus, since this model allows only diffusion of hydrogen to the crack tip as a result of a concentration gradient difference due to differing solvi concentrations at the two locations, it predicts no DHC even under cool-down conditions. Kim gets around this dilemma by stipulating – without quantifying the mechanism by which this is possible – that at $r = \ell$, the solvus (and not some effective concentration coming out of the steady-state diffusion solution as with the Dutton–Puls model) is reduced to that of TSSD because, when the bulk concentration is at TSSP, of all the hydrides that have nucleated everywhere in the sample only those in the plastic zone at the crack tip, somehow, when nucleated, lower the concentration there for subsequent hydride growth to exactly TSSD, i.e., the solvus concentration for hydride dissolution. (It is not clear, as stated in the main part of the paper, whether Kim appreciates that the various solvi have both a magnitude and a direction and, since TSSD applies to dissolving hydrides only, this assumption can only be sensible if it is only the magnitude of TSSP at the crack tip that has been reduced to that of TSSD.) The physical reasons why this would occur as well as why nucleation would, during each propagation step at constant temperature continue to occur spontaneously and at just the right spot in the plastic zone of the crack for the subsequent growth of these nucleated hydrides to grow together to a critical size for fracture is also not made clear by Kim.

None of such convoluted and questionable arguments are required to demonstrate what causes DHC with the various versions of the Dutton–Puls model, for which it has been shown unequivocally in Sections A.1–A.4 that it is the effect of stress on the chemical potential for hydrogen in solution that is the cause for DHC.

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