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Letter to the Editor

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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ABSTRACT

The aim of this work is a reply to Puls's paper entitled "Review of the thermodynamic basis for models of delayed hydride cracking (DHC) rate in zirconium alloys in J. Nucl. Mater. 393 (2009) 350–367" claiming that the thermodynamic basis of Dutton and Puls's model termed the first version of the old models is valid when compared to Kim's new model. The critical defect of the first version old model is to assume that the bulk hydrides are the source of diffusible hydrogen and the stress would decrease the crack tip concentration in solution even without hydride precipitation, creating the difference in hydrogen concentration or ΔC between the crack tip and the bulk. The latter assumption leads to predict DHC even at high temperature above 300 °C without a thermal cycle, demonstrating that the first version old model is unrealistic. The second version old DHC model assumes that the stress gradient is driving hydrogen to the crack tip, increasing the crack tip concentration over the bulk concentration, which is faulty because it violates the thermodynamic principle that tensile stresses lower the chemical potential of hydrogen or the hydrogen solubility. Despite the old models' claim that the driving force for DHC is the stress gradient, their analytical equations indicate that the crack growth rate (CGR) is governed by the ΔC, demonstrating that the driving force for the DHC is the ΔC, not the stress gradient.

1. Introduction

The author [1] has recently published a paper entitled "Review of the thermodynamic basis for models of delayed hydride cracking rate" claiming that Dutton and Puls's old model [2–4] termed the first version of the old delayed hydride cracking (DHC) models is valid and Kim's new DHC model [5–10] is incorrect. In fact, there are many unresolved issues related to DHC to date that the old DHC models cannot explain: the constant crack growth rate (CGR) with K_I, a rapid drop of the CGR above 300 °C, why DHC above 180 °C needs a thermal cycle but DHC below 180 °C occurs without it, and what determines the activation energy for the CGR and so on. Recently, using Kim's model, Kim has elucidated those unresolved issues the details of which have been recently published in the open literatures [5–13]. However, the author [1] claims that Kim's criticism about the old DHC models is unfounded, and has tried to show the rationale of how these unresolved issues can be explained by the old DHC models. The aim of this paper is to show that the author's claim [1] that Kim's criticism is unfounded is really unfounded and to demonstrate that Kim's model is valid.

2. Comment on the old DHC models

2.1. Driving force for hydrogen diffusion

For the first time, Dutton and Puls [2] presented an analytical model in 1975, 1 year after many pressure tubes had failed due to DHC in one of the Pickering nuclear power plants [14]. At that time, since DHC was not fully understood, it was thought that DHC could occur only at low temperatures where all the hydrides were present all over the specimen. It was not until 1978 that Simpson and Puls [15] reported that a thermal cycle was required to initiate DHC above 220 °C even though they could not explain the role of the thermal cycle in producing the reliable CGR. Given the limited understanding of DHC that occurred only in the presence of hydrides in the bulk and a crack tip, Dutton and Puls [2,3] claimed that the bulk hydrides were the source of hydrogen moving to the crack tip from the bulk, which is the most critical defect of their model. Evidence is found from Dutton's paper [3] quoted as saying that "it is energetically more favorable for hydrides to precipitate under the action of the high tensile stress within the hydrogen sink compared with a position in the matrix away from the crack. Thus, there exists a thermodynamic driving force for hydrides far from the crack to preferentially dissolve and precipitate at the crack tip." In other words, Dutton and Puls's model [2,3] was established to explain the so-called low temperature DHC [8] that was observed to occur below 180 °C even in isothermal conditions. The author [1] claims that the old DHC model proposed by Dutton and Puls [2,3] contains an analytical formulation but Kim's model does not have it. However, the so-called analytical model as claimed by the author [1] has nothing but the theoretical calculations of hydride solubility at the crack tip and in the bulk as shown in Eqs. (1) in this work and (8) in [2,3]:

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$$V = \frac{\pi\Omega_{hydride}}{1.6l'\Phi\Omega_{Zr}} D_H \Big\{ C_H^S \exp(p(L)\overline{V_H^h}/RT) \\ -C_H^S \exp(p(L)\overline{V_H^h}/RT)\exp(\Delta p\overline{V_H^h}/RT) \Big\} \quad (1)$$

where D_H is the diffusion coefficient of hydrogen, C_H^S the hydrogen solubility at zero stress, $p(L)$ and $p(l)$ are the hydrostatic stress at the source (bulk) hydrides and at the sink (crack tip) hydrides, Δp the difference in the hydrostatic stress between the bulk and the crack tip, and the others have the same meaning as in [2,3]. As shown in Eq. (1), their model has shown that the bulk and crack tip solubilities are determined only by the stress independent of the initial hydrogen concentration, which is fully unreasonable, and furthermore does not consider the effects of the yield stress, the threshold stress intensity factor or K_{IH} and the critical hydride length. Given these facts, it is clear that their analytical model is imperfect unlike the author's claim [1]. In contrast, Kim's model just uses either the experimentally determined hydrogen solvus lines as the local hydrogen solubilities at the crack tip and in the bulk or the initial hydrogen concentration if the cooling solvus is higher than the initial hydrogen concentration at any test temperature, and furthermore contains the explicit effect of the critical hydride length on the CGR that is determined by the yield stress and the K_{IH} [5–13]. Thus, as far as the local hydrogen solubilities at the crack tip and in the bulk are concerned, Kim's model [5–13] is more correct when compared to Dutton and Puls' model [1–4].

It should be noted that the first term of the bracket in Eq. (1) is the bulk hydrogen solubility and the 2nd term is the crack tip hydrogen solubility. Therefore, the bracket in Eq. (1) represents a difference in the hydrogen solubility between the bulk and the crack tip or ΔC. Thus, Eq. (1) can be expressed simply as a function of ΔC as such:

$$V = \frac{\pi\Omega_{hydride}}{1.6l'\Phi\Omega_{Zr}} D_H\{C_H(L) - C_H(l)\} = \frac{\pi\Omega_{hydride}}{1.6l'\Phi\Omega_{Zr}} D_H \Delta C_H \\ = k_1 D_H \frac{\Delta C}{l'} \quad (2)$$

where k_1 is a constant and l' is the effective crack tip radius that is assumed to be equal to the crack tip opening displacement. 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 [1] had to derive the revised model using the hydride interaction energy rather than the hydrogen interaction energy (see Eqs. (15), (18) and (19) of [1]):

$$V \propto [E_L - E_l] = \Delta C \quad (3)$$

with

$$E_L = C_H^{heat} \exp[\overline{w}_t^a(L)/RT], \quad (4)$$

and

$$E_l = C_H^{cool} \exp[\overline{w}_t^a(l)/RT] \quad (5)$$

Here, E_L, E_l, C_H^{heat} and C_H^{cool} are the bulk solubility and crack tip solubility, the experimentally determined solvi for hydride dissolution and precipitation under zero stress, respectively, and $\overline{w}_t^a(L)$ and $\overline{w}_t^a(l)$ are the hydride interaction energies at the dissolving and precipitating hydrides at L and l. Eqs. (4) and (5) indicate that the local solubilities at the crack tip and in the bulk are determined by the heating solvus and the cooling solvus, respectively, regardless of both *the initial hydrogen concentration* and *the direction to approach the test temperature*, which is totally invalid. Note that Eq. (3) has the same formula as Eq. (2), indicating that the ΔC is a driving force for the CGR. Similar statement was already made by Simpson and Puls [15] who had stated that "*the principal driving force giving rise to* Eq. (1) *is the difference in local hydrogen concentration between hydride platelets closed to and remote from the crack tip.*" Nevertheless, the author [1] has argued that this statement as shown above is misleading because the ΔC is a consequence of the action of the effect of the stress gradient on the chemical potential for diffusion of hydrogen. This is the author' rationale [1] claiming that the stress gradient is the driving force for DHC, which is unreasonable because the CGR is governed by the ΔC as clearly depicted in Eqs. (2) and (3).

According to the author's revised model [4] as shown in Eqs. (3)–(5), the stress always decreases the hydrogen solubility or hydrogen concentration in solution at a crack tip, leading it to be lower than the bulk solubility or hydrogen concentration in solution in the bulk or the ΔC to be formed between the bulk and the crack tip, driving hydrogen from the bulk to the crack tip. In other words, this revised model predicts that DHC can occur as long as the stress is applied locally only at the crack tip irrespective of the direction to approach the test temperature. This illogical rationale leads to predict that DHC can occur even at 350 °C and above upon an approach by heating as shown in Fig. 1, which is in contrast with the experimental fact that with the test temperature approached by heating, DHC cannot occur above 180 °C for the furnace-cooled Zr–2.5Nb alloy and above 250 °C for the water-quenched Zr–2.5Nb alloy as shown in Fig. 2 [8,16]. Direct evidence is provided by Simpson and Nuttal [17] who showed no precipitation of hydrides at a crack tip at 325 °C in isothermal conditions even under applied stresses but precipitation of hydrides at the crack tip after a thermal cycle between 325 and 380 °C as shown in Fig. 3. This faulty prediction of Puls's model, as shown in Fig. 1, results from the unreasonable assumption [1] that the crack tip acting as an open system in contact with a reservoir that has a higher chemical potential for hydrogen in solution receives hydrogen from the bulk, leading it to have a higher concentration than the reservoir. Note that the zirconium matrix with hydrogen is a closed system [18] because hydrogen cannot enter into or come out of the zirconium matrix. This invalid assumption results from the ignorance of the fact that a decrease in the hydrogen concentration at a crack tip due to the stress cannot occur kinetically without precipitation of hydrides. This is another defect of the old DHC models. In fact, they have never thought about precipitation or nucleation of the hydrides but just assume that *all the*

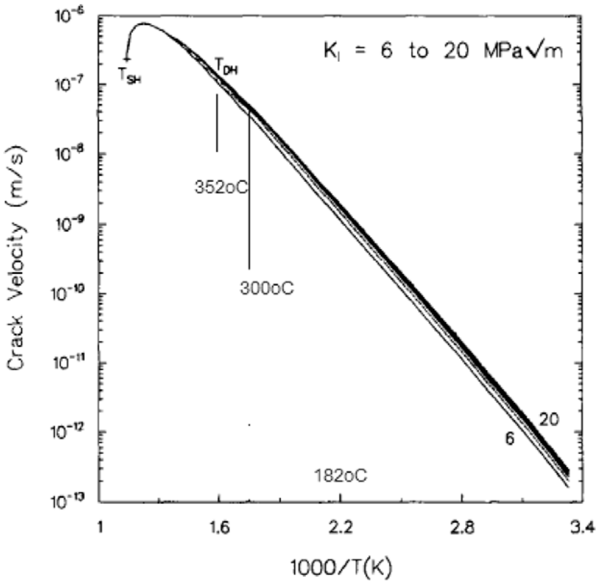

Fig. 1. Predicted crack velocity with temperature for a range of stress intensity factors (6–20 MPa $\sqrt{m}$) using Puls's model when the test temperature is approached by heating (taken from [4]).

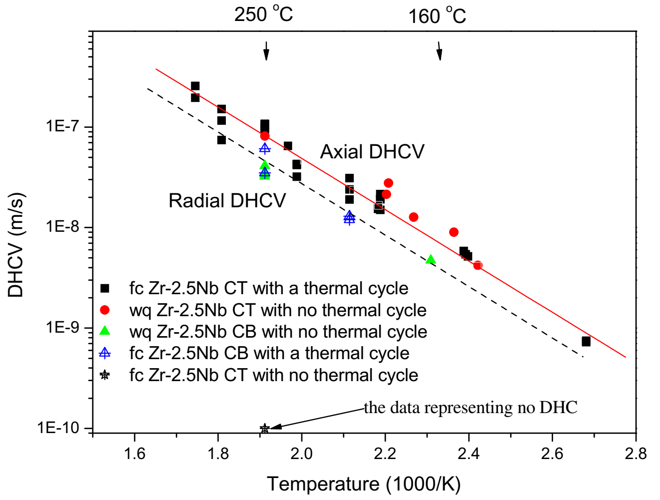

Fig. 2. Axial and radial delayed hydride crack velocity (DHCV) of the water-quenched and furnace-cooled Zr–2.5Nb specimens with and without a thermal cycle that were determined by using compact tension (CT) and cantilever beam (CB) specimens, respectively.

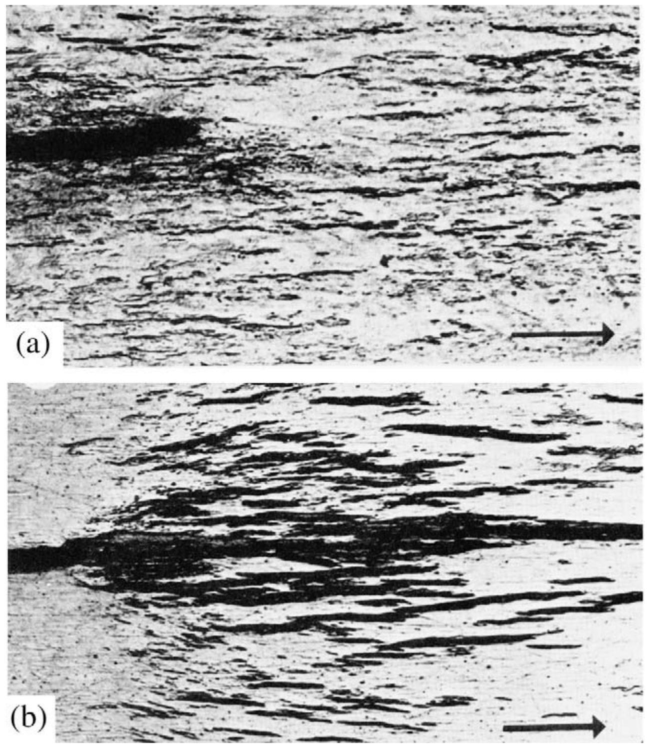

Fig. 3. Hydride distribution at a crack tip of a cold-worked Zr–2.5Nb at 325 °C: (a) after isothermal testing at 325 °C for 2000 h, and (b) after a thermal cycle between 325 and 380 °C. The arrow indicates the crack growth direction (taken from [17]).

hydrogen entering the crack tip region $r = l$ due to the hydrogen concentration gradient precipitates at the existing hydride [2,3].

An analogy is that milk cannot come out of the milk box despite a pumping force being applied through a straw if it is a closed system where the milk cannot enter into or come out of it. However, if the milk box shrinks by pressing with hands, then milk comes out of it very easily. Likewise, 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. This explains why the stress cannot move hydrogen to the crack tip in isothermal conditions without cooling. Evidence is provided by Kammenzind's experiment [19] 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 the constant stress. However, after 25 thermal cycle treatments with cooling from the peak temperature, the stressed region had a higher concentration than the unstressed regions due to precipitation of hydrides in the stressed regions during cooling. Kammenzind's experiments [19] have clearly demonstrated that a hydrogen transfer occurs only on cooling where the bulk volume shrinks hydrostatically. Consequently, it is evident that the author's assumption [1] that the crack tip acts as an open system and the stress causes diffusion of hydrogen is faulty.

2.2. Constant CGR independent of K_I

One of the critical defects of the old models is that they cannot explain the constant CGR independent of K_I and rather predicts a reduction of the CGR with K_I as shown in Fig. 4 [20]. This occurs because the old models have claimed the stress driven flow of hydrogen to the crack tip, which is one of Kim's critical criticism on the old DHC models. Nevertheless, The author's remark [1] quoted as saying that "*Kim agrees that there is a dependence on stress of the chemical potential for diffusion of hydrogen in a metal*" seems to distort Kim's model [5–13]. It should be noted that the stress just decreases the chemical potential of hydrogen itself, not the chemical potential for diffusion of hydrogen. In [1], however, it seems that the author would like to highlight the role of stresses in changing the chemical potential for diffusion of hydrogen, which is claimed to be the driving force for hydrogen diffusion. However, this claim is totally unreasonable because it is the gradient of chemical potential, not the chemical potential for hydrogen diffusion to cause diffusion of hydrogen. In other words, as the chemical potential of hydrogen itself has nothing to with hydrogen diffusion, it is clear that stress, just decreasing the chemical potential of hydrogen theoretically, has nothing to do with hydrogen diffusion. As shown in Eqs. (1) and (3)–(5) the old DHC models have assumed that the bulk and crack tip solubilities have a dependence on the stress, causing the ΔC to change with the stress irrespective of the initial

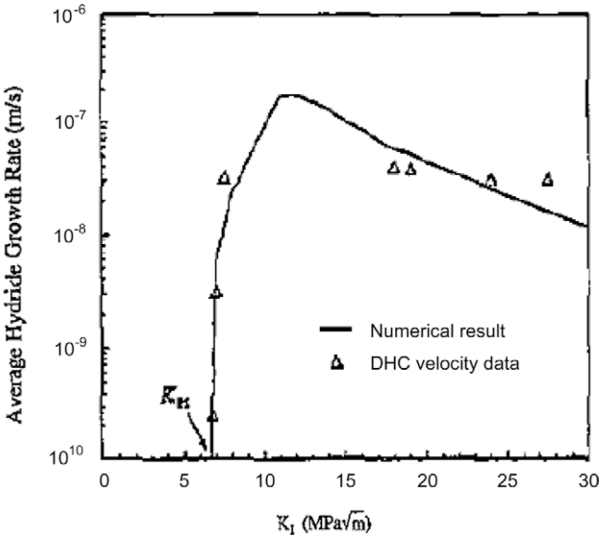

Fig. 4. The predicted hydride growth rate with K_I using the second version old model [20].

hydrogen concentration contained in the specimen. This explains why the old DHC models have always predicted the CGR to change with the stress, irrespective of the initial concentration as shown in Fig. 4. In contrast, according to Kim's model [5–13], the ΔC becomes constant independent of the stress but changes with the initial hydrogen concentration. This occurs because the crack tip solubility is lowered to the equilibrium solubility at any given test temperature (or C_d as shown in Fig. 5) due to the so-called stress induced precipitation of hydrides [6], but the bulk solubility follows either the initial hydrogen concentration (C_o) or the cooling solvus or $C_p(T_t)$ (Fig. 5) at the test temperature (T_t), depending on if the former is less or more than the latter, respectively. It should be noted that the ΔC, corresponding either to the distance BC when C_o is less than $C_p(T_t)$ or to the distance B′C′ when vice versa as shown in Fig. 5, is constant independent of the stress. This explains why the CGR of a Zr–2.5Nb tube became independent of the stress at any temperature and increased linearly with the ΔC as shown in Fig. 6 [11]. Despite the author's claim [1] that the old DHC model has an analytical formula, he has not provided an analytical explanation for the effect of the stress on the CGR using his model but described it in a qualitative manner. The author [1] has argued that by eliminating a dependence of the hydride thickness with K_I and by keeping the distance where the bulk concentration in solution is constant close to the crack tip, the effect of K_I on the CGR has essentially been eliminated [1]. It should be noted that this argument is advanced without any quantitative rationale. In support of this argument, however, the author [1] has cited the prediction of Puls's revised model [4] that the DHC rate changes little with K_I, as shown in Fig. 1. Given that this model is full of the faulty assumptions enough to predict the initiation of DHC even at and above 350 °C upon an approach by heating (Fig. 1), it is very hard to accept the validity of the author's argument [1] that the old DHC model can explain little K_I dependence of the CGR. The author [1] should have shown the predicted results demonstrating the constant CGR independent of K_I using the realistic DHC model that can explain all the other issues related to DHC. Furthermore, using the above-argument, the author [1] claims that why a material with a higher yield strength would have a higher DHC propagation rate is due to the increased plastic stress in the plastic zone with increasing yield strength that would increase the stress-driven diffusion rate. Note that this author's claim [1] is qualitatively proposed without referring to his analytical equations. Considering Eqs. (3)–(5) indicating that the stress just affects the local hydrogen solubilities, not hydrogen diffusion, however, the claim that the plastic stress increases the stress-driven diffusion rate is questionable. In fact, given Eqs. (3)–(5), the stress effect on the CGR would be negligible, which may explain the minor effect of the applied stress effect on the CGR but cannot rationalize a strong dependence of the CGR on the yield strength of the zirconium alloys. Consequently, the first version old model cannot consistently explain the stress dependence of crack growth rate in zirconium alloys.

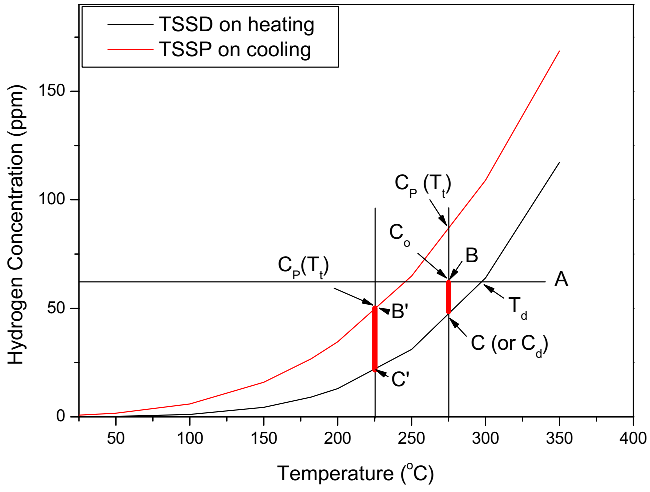

Fig. 5. The bulk and crack tip solubilities depending on the initial concentration of the specimen, C_o when compared to the cooling solvus at the test temperature [$C_p(T_t)$]. The driving force ΔC is either the distance BC when C_o is less than $C_P(T_t)$ or the distance BC when vise versa, respectively.

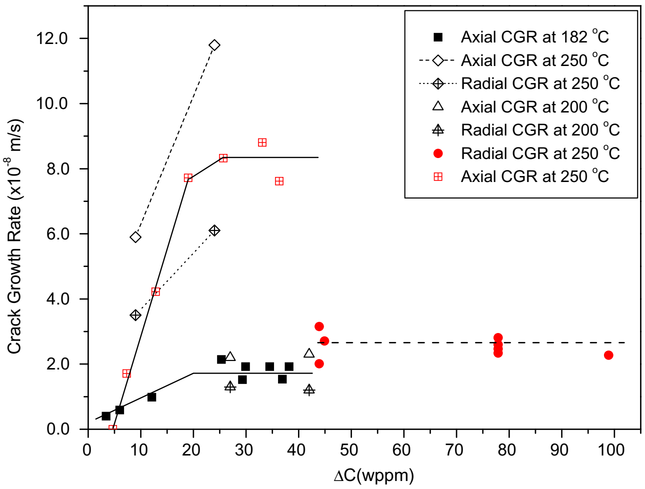

Fig. 6. Dependence of the crack growth rate on supersaturation of hydrogen ΔC that is obtained by the initial hydrogen concentration subtracted by the heating solvus at a test temperature [11].

2.3. Effect of the direction approaching the test temperature on DHC

DHC is well known to depend on the direction of approaching the test temperature [8,16]: with the test temperature approached by heating, DHC is arrested at a critical temperature above 180 °C for the furnace-cooled Zr–2.5Nb specimen and 250 °C for the water-quenched specimen but, with the test temperature approached by cooling, DHC arrest occurs above 300 °C. Using Dutton and Puls's model [2,3], Ambler [16] suggested the cause of the DHC arrest to be due to the ΔC being reduced to zero irrespective of the direction of approaching the test temperature, leading to theoretically determine the DHC arrest temperatures. By citing Ambler's work, the author [1] has claimed that the old model can explain DHC arrest. Given that the ΔC is related to nucleation of hydrides [11,13], the author's claim [1] that the ΔC being reduced to zero is the cause of the DHC arrest above 300 °C would be as if no nucleation of hydrides were the cause of the DHC arrest above 300 °C. Strong evidence against the author's claim [1] is provided by Resta Levi and Puls [21] who have shown the hydrides nucleated at the tip of a crack that have been arrested despite an approach by cooling. Thus, it is clear that the author's claim [1] that the old DHC model can explain the effect of the direction approaching the test temperature on DHC is unreasonable.

2.4. Crack tip concentrations

There are two different kinds of old DHC models claiming that the stress gradient is the driving force: one is the so-called first version model [2–4] claiming that the bulk hydrides are the source of hydrogen which can diffuse from the bulk to the crack tip, and the other is the second version model [20,22,23] claiming that the source of diffusible hydrogen is not the bulk hydrides but hydrogen in solution in the zirconium matrix. As far as the source of hydrogen is concerned, the first version old model is erroneous because DHC occurs even in the absence of the bulk hydrides. Note that the first version model including all the old models proposed by Dutton et al. [2–3] and Puls [4,15] have assumed that the crack tip concentration is always lower than the bulk concentration as delineated in Eqs. (2) and (3) while the second version model suggested by Eadie [22] and Shi et al., [23] has assumed that the crack tip concentration is higher than the bulk concentration. Thus, the crack tip concentration turns out to be different between the two models: it is reduced to close to the TSSD for the first version model [24] while it increases to the TSSP for the second version model [23]. Despite the author's argument [1] that *Puls's revised model 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 tensile stress*, however, Eq.3 demonstrates that the crack tip concentration must be lower than the bulk concentration. Thus, the author's argument [1] that Puls's revised model [4] accounts for the case with the crack tip concentration being higher than the bulk concentration must be erroneous.

The big assumption of the second version DHC model is that the crack tip concentration is increased over the bulk concentration to the TSSP due to the stress effect. Given the effect of tensile stresses that decreases the chemical potential of hydrogen as in [1,6,18]:

$$\Delta\mu_H^{\sigma>0} = \Delta\mu_H^0 - \sigma V_H^h, \tag{6}$$

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 σV_H^h corresponds to the so-called hydride interaction energy [1], the stressed region or the crack tip 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:

$$\Delta\mu_H^0 = \mu_H^D - \mu_H^0 = RT\ln C_H^D \tag{7}$$

where μ_H^0 is the chemical potential at the reference level, T temperature and C_H^D is 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 follows:

$$C_H^D \text{ at a crack tip} < C_H^D \text{ in the bulk} \tag{8}$$

Hence, the second version model claiming that the crack tip concentration is increased over the bulk concentration violates the thermodynamic principle as in Eq. (8), demonstrating that the second version DHC model is an unrealistic model.

The 2nd assumption of the second version old model is that the crack tip concentration can increase to the TSSP due to the stress. However, according to Kim, the crack tip concentration cannot reach the TSSP when the bulk concentration remains at the TSSD as with the test temperature being approached by heating, which cannot explain the so-called low temperature DHC that occurs below 180 °C upon an approach by heating. This occurs because the increments of the crack tip concentration due to the stress effect are always less than the ratios of the TSSP over the TSSD at any given temperatures [8,12]. According to Puls's theoretical calculation as shown in Table 1 [25], the predicted increase in hydrogen solubility (or C_H/C_H^o) due to the tri-axial stresses applied at the crack tip ranges from 1.65 to 1.18 over a temperature range of 300 to 600 K. However, the measured ratios of the TSSP over the TSSD ranging from 6.25 to 1.28 are always higher than the predicted ratios of C_H/C_H^o at any given temperature. It should be noted that the ratio of the TSSP over the TSSD becomes larger with decreasing temperature, showing that the possibility that TSSP can be reached from TSSD is much less at lower temperatures even under the same tri-axial stresses. Here, it should be noted that the ratios of the TSSP over the TSSD in the 3rd row of Table I are determined using the measured values of hydrogen solubilities of Zr–2.5Nb for formation and dissolution of hydrides, respectively, both of which were reported by Pan [26]. Kim [12] has also shown the similar results to those shown in Table 1, as shown in Fig. 7: the measured ratios of the TSSP over the TSSD are always higher than the calculated ratios of C_{max}/C_o by Shi et al. [23] where C_{max} and C_o correspond to the crack tip hydrogen concentration and the bulk hydrogen concentration, respectively. Consequently, it is clear that as long as the bulk hydrogen concentration remains at the TSSD as with the test temperature being approached by heating, the crack tip hydrogen concentration cannot increase to the TSSP at any stresses being applied to the crack tip, leading to no precipitation of hydrides at the crack tip and hence to no DHC. This is the rationale why Shi et al. [23] has claimed that DHC is arrested when the bulk concentration corresponds to the TSSD. The author [1] has also conceded our point by stating that the solvus concentration cannot be exceeded at as low a temperature as 373 K. Nevertheless, he has claimed that using an arbitrarily lower value for hydrogen strain energy would increase the predicted value for the solvus concentration for dissolution, causing the TSSP to be exceeded due to an amplification of the hydrogen concentration caused by the stress gradient [1].

Table 1
The predicted ratios of C_H/C_H^o (crack tip solubility over the bulk solubility) due to applied stresses at a crack tip and the measured ratios of TSSP over TSSD in Zr–2.5Nb tube with temperature.

Temperature (K)	300	400	500	600
Predicted C_H/C_H^o [25]	1.65	1.4	1.27	1.18
Measured TSSP/TSSD [26]	6.25	2.83	1.76	1.28

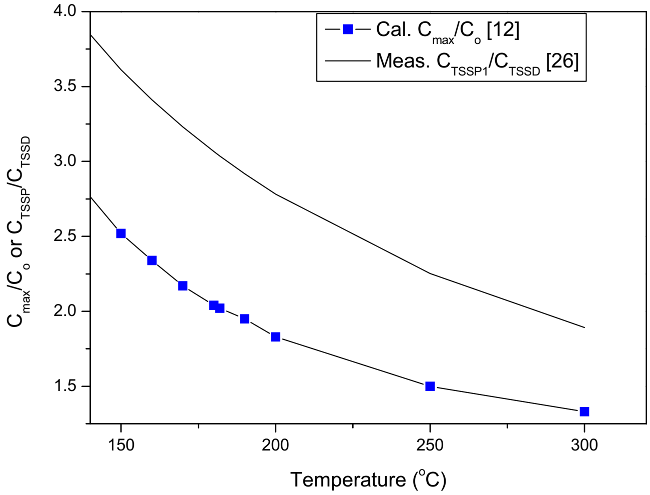

Fig. 7. Comparison of the calculated ratios of the maximum hydrogen concentration at the crack tip, C_{max} over the hydrogen concentration, C_o in the bulk region due to applied tensile stresses in the Zr–2.5Nb tube [9] with the measured ratios of C_{TSSP} over C_{TSSD} for the Zr–2.5Nb tube [26] (taken from [12]).

3. Kinetics of crack growth by DHC

According to Cann and Sexton's experiment [27], hydrides nucleated at a notch tip even at room temperature, grew to a critical length and cracked, thereby causing a crack to grow. This fact has clearly demonstrated that DHC involves the three consecutive processes such as nucleation, growth and cracking of hydrides at the tip of a notch or a crack. Therefore, it is clear that nucleation of hydrides is the first step of DHC. However, despite the same observation that hydrides nucleate in the stressed regions of zirconium alloys, all the old DHC models [1–4,15,20–23] proposed so far have assumed that the 1st process of DHC is diffusion of hydrogen to a crack tip of a higher stress from the bulk under the stress gradient, not nucleation of hydrides. Hence, they have assumed that DHC is diffusion controlled process so that the CGR is claimed to be governed only by the hydride growth rate. In contrast, according to Kim's DHC model [11,13], the CGR is determined not simply by the hydride growth rate but by the rate of the slowest process among the three processes involved in DHC such as nucleation, growth and cracking of hydrides. Considering this fact, the old DHC models' claim that DHC is diffusion controlled process is too simple an assumption to understand DHC of zirconium alloys. The old DHC models' claim that hydrogen diffusion is the first process of DHC would be as if hydride nucleation governs the CGR in view of kinetics because hydrogen diffusion just determines the rate of hydride nucleation. To overcome this problem, the author [1] has assumed that the time required for the crack tip concentration to increase to the TSSP is negligible compared to the time for the nucleated hydrides to grow to a critical size. Given their assumption that hydrogen diffusion determines not only the time for the crack tip concentration to reach the TSSP for nucleation of hydrides but also the time for nucleated hydrides to grow to the critical length, the author's claim [1] that the former process or the nucleation process is much faster than the latter process or the growth process is unreasonable.

Given that the second phase particles of a higher molar volume can nucleate in metals with a lesser molar volume only under supersaturation of solutes [28], nucleation of hydrides occurs only under hydrogen supersaturation or ΔC. For example, the ΔC in zirconium alloys with a constant hydrogen concentration can be achieved by applying a thermal cycle where the test temperatures above 180 °C are approached by cooling above the TSSD temperature. This explains why DHC above 180 °C occurs only with a thermal cycle: without a thermal cycle, no hydrogen supersaturation is created, leading to no nucleation of hydrides, as shown in Fig. 3a. Below 180 °C, however, the supersaturation of hydrogen 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 [8,29]. This explains why DHC occurs without a thermal cycle below 180 °C. This fact indicates that despite an approach to the test temperature by heating where the bulk and the crack tip have the same solubility as the TSSD, DHC occurs. Consequently, the driving force for DHC is either the supersaturation of hydrogen or ΔC above 180 °C or the difference in hydrogen concentration in solution between the bulk and the crack tip resulting from the higher solubility of the γ-hydride when compared to that of the δ-hydride.

The author [1] criticized Kim's low temperature DHC model by claiming that the assertion of a higher solvus concentration for gamma dissolution compared to that for delta hydride dissolution is highly speculative without experimental evidence. Note that as concrete evidence for the stress-induced hydride phase transformation, for the first time, we have demonstrated using X-ray diffraction analyses that the hydride phase on the fracture phase and in the bulk is the δ- and γ-hydrides, respectively, as shown in Fig. 8. To explain the DHC arrest at 180 °C, Ambler [16] also assumed that the crack tip hydride was the δ-phase while the bulk hydride was the δ-phase for the furnace-cooled specimens and the γ-phase for the water-quenched one without any physical evidence. Despite Ambler's assumption being hypothetic [16], his conjecture agrees partly with our observation shown in Fig. 8. Nevertheless, the author [1] has argued that the results of Fig. 8 are unconvincing without presenting any concrete proofs refuting them. In addition, the author [1] has denied the experimental facts [30–35] shown in Fig. 9 [8,36], demonstrating that the γ-hydride is a stable phase with a higher solubility of hydrogen than the δ-hydride by referring to the unilateral criticism of Ritchie [37] on the data reported by Cann and Atrens [30] and by Mishra and Asundi [31]. Given that five kinds of measured data set regarding the solubilities of the gamma and delta hydrides which have been determined by five different scientists fall together, as shown in Fig. 9, Kim's claim [8,36] that the gamma hydride has a higher solubility that the delta hydride is more evident. More direct evidence for a higher hydrogen of

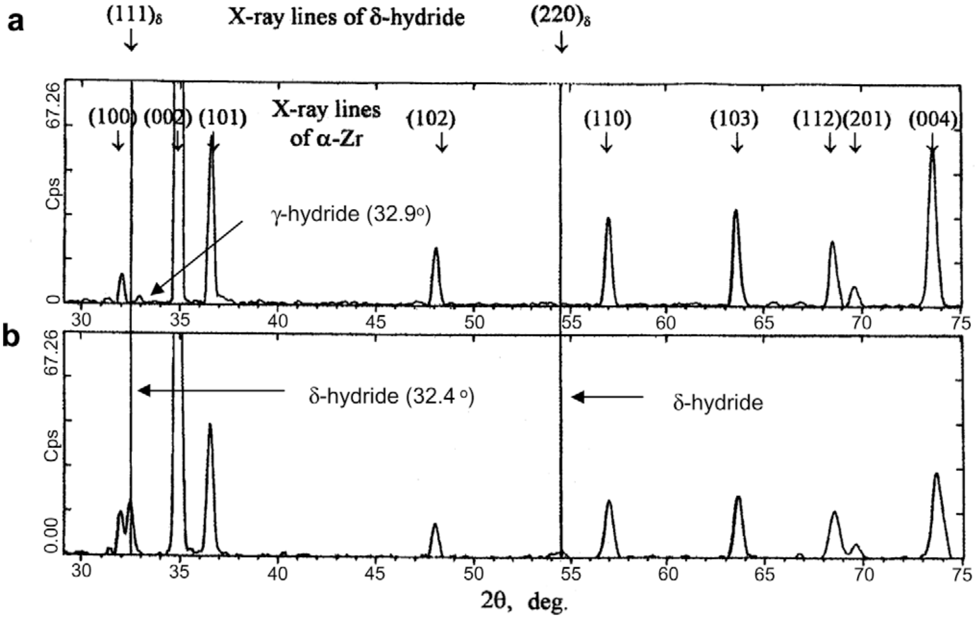

Fig. 8. X-ray diffraction analyses of (a) the bulk region at a distance of 20 mm from the crack tip and of, and (b) the crack tip in the water-quenched Zr–2.5Nb specimens subjected to a DHC test at 250 °C [36].

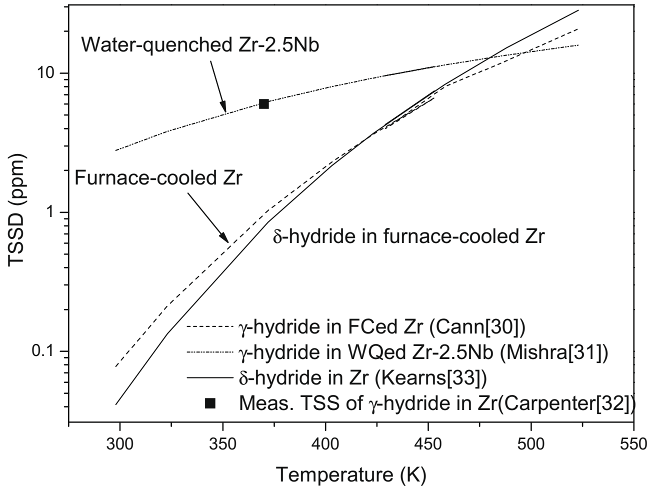

Fig. 9. Terminal solid solubility (TSS) of the γ-hydride in the furnace-cooled Zr–2.5Nb (Cann [30]) and in the water-quenched zirconium (Mishra [31]) and of the δ-hydride determined from Kearns data along with the measured TSS of the γ-hydride in water-quenched Zr (Carpenter [32]) (taken from [8]).

the γ-hydride is provided by Root and Fong's in situ experiment [38] demonstrating that specimen *A* with a higher volume fractions of the γ-hydride has a higher solubility on heating when specimen B with a lower volume fractions of the γ-hydride whose solubility has fallen on the Kearns solvus line as shown in Fig. 10. Note that since specimen A was stored at RT for 2 years after charging of hydrogen [38], the concentration of the γ-hydride in specimen A has increased with time even at room temperature due to hydride phase transformation from δ to γ [36] when compared to specimen B that has not been stored at RT. The author's claim [1] that the formation of the γ-hydride in favor of the δ-hydride is associated with differences in kinetic requirements during rapid cooling is just speculative without concrete evidence. The stability of the hydride phase is evidenced by the in situ measurements of a change in the volume fractions of the two hydride phases with annealing time at low temperatures below 180 °C corresponding to the γ–δ phase transformation. Root [39] has demonstrated that it is the γ-hydride that increases in volume at the sacrifice of the δ-hydride with annealing time at as low a temperature as 50 °C, as shown in Fig. 11. Definitive evidence is found from Khatamian's observation [40] that long-time annealing of the furnace-cooled Zr–2.5Nb specimen with hydrogen at 150 °C has produced the specimen with only the γ-hydride without the δ-hydride.

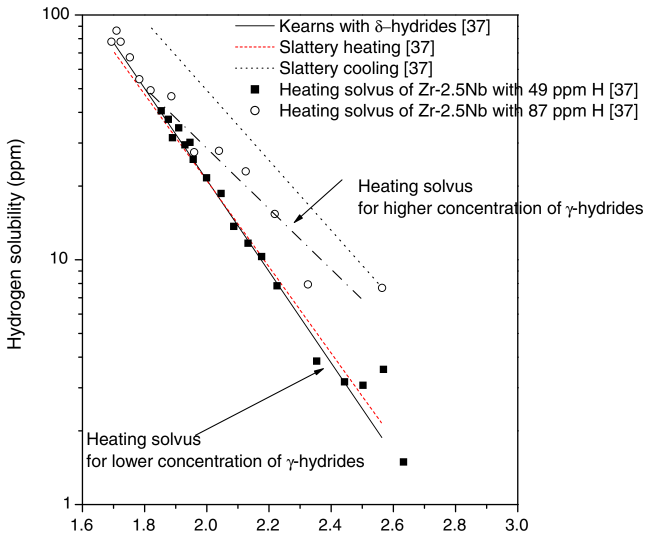

Fig. 10. Heating solvus of the Zr–2.5Nb specimens with the concentration of γ-hydrides that were determined by neutron diffraction [37], demonstrating that the Zr–2.5Nb specimen with 87 wppm H had higher solubility of hydrogen due to a higher concentration of the γ-hydride when compared to that with 49 wppm H (taken from [37]).

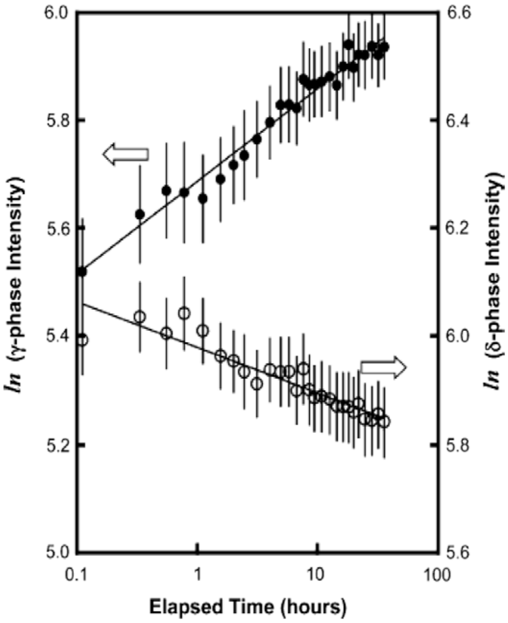

Fig. 11. Change of the hydride (1 1 1) diffraction peak integrated intensity versus time showing growth of the gamma hydride and decay of the delta hydride in the Zr–2.5Nb specimen with annealing time at 50 °C [39].

As DHC at low temperatures occurs due to the γ–δ phase transformation according to Kim's model, DHC must be arrested above the γ–δ phase transformation temperature due to the absence of the γ-hydrides with a higher solubility. Evidence is provided by the experiments by Kim [8] and Ambler [16] demonstrating a rapid drop of the CGR above 180 °C for the furnace-cooled specimens, and above 250 °C for the water-quenched specimens. Given the fact that the γ- to δ-hydride phase transformation temperature corresponds to 182 °C for the furnace-cooled specimens [36,38] and to 255 °C for the water-quenched specimens [31], it is clear that DHC at low temperatures on heating occurs due to the presence of the γ-hydride with a higher solubility of hydrogen. Given this fact, it is clear that the γ-hydride is a stable phase at low temperatures. However, regarding this fact, no plausible explanation has been provided in [1]. Hence, this is supportive evidence demonstrating the validity of Kim's model.

4. Conclusions

Despite the fact that DHC of zirconium alloys involves nucleation, growth and cracking of hydrides, all the old DHC models have assumed that the first process of DHC is diffusion of hydrogen, not the nucleation of hydrides so that the CGR (or DHC rate) is governed solely by hydrogen diffusion controlled process, which is the most critical defect of the old DHC models. The first version old model established by first Dutton and later Puls was advanced to explain the so-called low temperature DHC leading to assume that the source of diffusible hydrogen is the bulk hydrides. The critical defects of this first version old model is the assumption that the bulk hydrides are the source of hydrogen and the stress would decrease the crack tip concentration in solution even without hydride precipitation, causing the ΔC to be established between the crack tip and the bulk. The latter assumption led the first version old model to predict DHC even at high temperatures above 300 °C without a thermal cycle, which is unrealistic. The second version old model assumes that the source of hydrogen is hydrogen in solution and hydrogen moves under the stress gradient, increasing the crack tip concentration to the cooling solubility. However, the latter assumption of higher crack tip concentration in solution than the bulk concentration turns out to violate the thermodynamic principle that applied stresses lower the chemical potential of hydrogen or the hydrogen solubility, which is the most critical error of the 2nd version model. Although both the old models qualitatively claims that the driving force for DHC is the stress gradient, their analytical equations indicate that the CGR is governed by the ΔC, demonstrating that the driving force for DHC is the ΔC, not the stress gradient, which is the main idea of Kim's model.

In contrast, given the processes involved in DHC of zirconium alloys, Kim's model indicates that the first process of DHC is hydride nucleation, not diffusion of hydrogen. Furthermore, it shows that the crack grow rate is governed solely not by the rate of hydride growth but by the rate of the slowest process among the three consecutive processes. Hence, the driving force for DHC according to Kim's model is the concentration difference or ΔC between the bulk and the crack tip due to either stress induced precipitation of hydrides above 180 °C or stress induced phase transformation from γ to δ below 180 °C. One of the strongest points of Kim's model is that it explains all the unresolved DHC issues.

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