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Review

Author's 2nd reply to 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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ABSTRACT

The aim of this work is a second reply to Puls's comments on the author's first reply to the paper published in J. Nucl. Mater. 393 (2009) 350–367. The Dutton–Puls model indicates that the CGR is governed not by the stress gradient but by the ΔC that results from a decrease in the crack tip solubility due to the stress when compared to the bulk solubility, demonstrating that Puls's defense of the Dutton–Puls model is inconsistent and invalid. Given the fact that DHC involves three consecutive processes such as nucleation, growth and cracking of hydrides at the crack tip, Puls's claim that DHC is simply a diffusion-controlled process and the CGR is governed solely by the rate of hydride growth is incorrect, yielding many of the unsolved issues related to DHC. It is confirmed that Kim's criticism that the Dutton–Puls model for the crack growth rate (CGR) is established based on a faulty thermodynamic basis is correct.

Contents

1. Introduction

This work is to reply to Puls's rebuttal [1] to Kim's criticisms [2] of the old delayed hydride cracking (DHC) models including the Dutton–Puls model.

2. Comments on the Dutton–Puls model

2.1. Driving force

The author [2] has commented that the critically defective assumptions of the Dutton–Puls model are that the hydrides must be present in the bulk to supply diffusible hydrogen to the crack tip and the DHC rate or the crack growth rate (CGR) is governed solely by the hydride growth rate disregarding the effects of nucleation and cracking of hydrides. As a rebuttal, Puls [1] has said that "*all of the claimed limitations of the Dutton–Puls model that were pointed out by Kim are eliminated by making a change to the boundary conditions in the Dutton–Puls model.*" Nevertheless, the change to the boundary conditions still focuses on the theoretical calculations of the local concentrations in solution or the local solvi at the crack tip and in the bulk, still ignoring not only the rates of nucleation and cracking of hydrides but also the effects of the yield stress, the threshold stress intensity factor or K_{IH} and the critical hydride length. Thus, all the so-called analytical equations for the CGR that has been derived by either Dutton and Puls or Puls as shown in

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Eq. A24, A27, A35 [1], Eqs. (1)–(5) [2] show that the CGR termed V is governed simply by the difference between the local solvi or local hydrogen concentrations in solution in the stressed and unstressed regions as shown in Eq. (1) [3]:

$$V \propto [E_L - E_l] = k\Delta C \tag{1}$$

where k is a constant that has nothing to do with the yield stress but changes with the diffusivity of hydrogen D_{H} and the effective crack tip radius [4,5] or the effective hydride thickness [6], E_L is the hydrogen concentration in the bulk termed the bulk solubility [1–3,5]

$$E_L = C_{\mathrm{H}}^{heat} \exp[\overline{w}_t^a(L)/RT] \tag{2}$$

and E_l is the hydrogen concentration at the crack tip termed the crack tip solubility

$$E_l = C_{\mathrm{H}}^{cool} \exp[\overline{w}_t^a(l)/RT] \tag{3}$$

where C_{H}^{heat} is the terminal solid solubility for hydride dissolution (TSSD), $C_{\mathrm{H}}^{cool}$is the terminal solid solubility for hydride precipitation termed TSSP1, and $\overline{w}_t^a(L,l)$ is the work term given by the applied stress or the hydride interaction energies at the dissolving and precipitating hydrides at L and l [3]. Despite Puls's claim [1,3] that the driving force for DHC is the stress gradient, his analytical equations (Eqs. (1)–(3)) demonstrate that hydrogen diffuses from the bulk to the crack tip due to the concentration gradient or ΔC, not due to the stress gradient. Given McRae's model [7] showing that the CGR is also determined by the ΔC [8], thus, it is evident that all the old DHC models demonstrate that the ΔC is the driving force for DHC. In other words, unlike Puls' claim that the stress gradient is the driving force for DHC, all the analytical equations derived by all the old DHC models demonstrate that the ΔC is the driving force for DHC, proving that Puls's claims are inconsistent and incorrect. Note that Dutton and his workers [4,5] and Simpson and Puls [9] have already indicated that *hydrogen moves to the crack tip region due to the concentration gradient*, not due to the stress gradient.

2.2. Limitations of the Dutton–Puls model

The technical background behind the Dutton–Puls model is that this model was established to explain the so-called low temperature DHC where DHC would be believed to occur in the presence of the hydrides lying circumferentially without a thermal cycle [2], which was also conceded by Puls [1]. This explains why the Dutton–Puls model assumed that the bulk hydrides were the source of diffusible hydrogen according to the invalid hypothesis supposing [4,5] that "*there exists a thermodynamic driving force for hydrides far from the crack to preferentially dissolve and precipitate at the crack tip*." In other words, this limited understanding of DHC at that time led them to predict that whenever the stress is applied only to a crack tip, according to Eqs. (1)–(3), the crack tip solubility always becomes smaller due to the hydride interaction energy than the bulk solubility even without precipitation of hydrides, creating the difference in the concentration between the bulk and the crack tip. Actually, McRae et al. [7] has claimed that the Dutton–Puls model is a kind of the precipitation first model (PFM) because a decrease of the concentration at the crack tip due to the stress cannot occur without precipitation of hydrides, indicating the invalidity of Puls's claim that the hydrogen concentration at the crack tip instantaneously decreases due to the applied stress, as explicitly shown in Eq. (3). This hypothesis is one of the critical defects of the Dutton–Puls model, leading Puls [6] to predict that DHC could occur above 300 °C even in isothermal conditions (Fig. 1 in [2]). However, it is unrealistic and inconsistent with the experimental facts that DHC is seen not to occur without a thermal cycle above 180 °C as evidenced by the author [2] and the others [10–12] (Fig. 3 in [2]). In short, the inherent limitation of the Dutton–Puls model is that it was developed to explain the low temperature DHC that is seen to occur in the presence of hydrides even without a thermal cycle, not the high temperature DHC occurring only in the thermal cycle in the absence of hydrides. Given this limitation, Puls's claim that the Dutton–Puls model accounts for nucleation of hydrides at the crack tip by increasing the crack tip concentration to the cooling solvus or TSSP1 is questionable.

2.3. Crack tip concentration

One of the controversies between Kim's model [12–20] and the old DHC models [1,3–7] is the crack tip concentration: the former demonstrates that the crack tip concentration is equal to the heating solvus or TSSD but the latter claims that it should be increased to the cooling solvus termed TSSP1. In fact, despite Puls's claim that *Kim's model where the crack tip concentration is reduced by the stress effect than the bulk concentration is erroneous*, it is seen according to Eqs. (1)–(3) that the crack tip concentration E_l which is less than the cooling solvus C_{H}^{cool} due to the stress effect is lower than the bulk concentration E_L. Thus, it is demonstrated that it is Puls's claim, not Kim's model that is erroneous, according to the Dutton–Puls model. The author [2] criticized that the Dutton–Puls model did not think about nucleation of hydrides at the crack tip and just assumed that all the hydrogen entering the crack tip region precipitates at the existing hydrides. As a rebuttal to this criticism, Puls [1] has claimed that "*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*." However, the growth of the existing hydrides lying circumferentially by the diffusion of hydrogen from the bulk has nothing to do with DHC. It is the reoriented hydride lying radially that should be nucleated at the crack tip to initiate DHC, which has never been considered in the Dutton–Puls model [4,5]. Besides, unlike Puls's claim, the crack tip solubility cannot reach the TSSP1 or C_{H}^{cool} because E_l is always less than C_{H}^{cool}, as clearly shown in Eq. (3). Thus, Puls's claim [1,3] that the Dutton–Puls model has considered nucleation of the reoriented hydrides implicitly as a first step is totally incorrect.

Against the author's statement [12–20] that the crack tip concentration is reduced to the TSSD at equilibrium, they have claimed that the cooling solvus cannot change with the stress so that hydrides can precipitate only when the crack tip concentration increases to the TSSP1 [1,3,7]. This misconception results from the ignorance of stress-induced precipitation of hydrides as experimentally evidenced by Kim [2,13], Birnbaum and his co-workers [21,22] and Westlake [23]. According to Eq. (3), the crack tip solubility or the hydrogen concentration in solution at the crack tip is lower than the TSSP1 due to the hydride interaction energy despite no change in the cooling solvus with the stress. Furthermore, Puls [24] himself showed theoretically that *the effective terminal solid solubility (TSS) for the crack tip hydride is reduced to the stress-free TSS or the heating solvus (TSSD) due to the applied stress*. Thus, Puls's claim [1] that the crack tip solubility should increase to C_{H}^{cool} to precipitate hydrides at the crack tip is also incorrect.

Regarding Puls's remark [1] that "*Kim does not indicate how he arrives at the results in Eq.* (3) *with the use of Eqs.* (1) *and* (2) [2]," the author kindly explains how it is derived as below:

Substituting μ_{H}^0 given by Eq. (2) [2] into Eq. (1) [2] yields Eq. (4), as Puls [1] does:

$$\Delta\mu_{\mathrm{H}}^{\sigma>0} = RT\ln C_{\mathrm{H}}^D - \sigma V_{\mathrm{H}}^h \tag{4}$$

The chemical potential in the stressed region or $\Delta\mu_{\mathrm{H}}^{\sigma>0}$ is expressed as in:

$$\Delta\mu_{\mathrm{H}}^{\sigma>0} = RT\ln C_{\mathrm{H}}^{D\sigma} \tag{5}$$

By equating Eqs. (4) and (5), we obtain Eq. (6)

$$\Delta\mu_{\mathrm{H}}^{\sigma>0} = RT\ln C_{\mathrm{H}}^{D} - \sigma V_{\mathrm{H}}^{h} = RT\ln C_{\mathrm{H}}^{D\sigma} \tag{6}$$

where C_{H}^{D} and $C_{\mathrm{H}}^{D\sigma}$ are the diffusible hydrogen concentrations in the bulk and at the crack tip, respectively. From Eq. (6), $C_{\mathrm{H}}^{D\sigma}$ is expressed as shown in:

$$C_{\mathrm{H}}^{D\sigma} = C_{\mathrm{H}}^{D}\exp\left(-\frac{\sigma V_{\mathrm{H}}^{h}}{RT}\right) \tag{7}$$

Thus, the hydrogen concentration in the stressed region or at the crack tip is reduced than that in the bulk by the work term given by the stress or $\exp\left(-\sigma V_{\mathrm{H}}^{h}/RT\right)$, showing that the author's statement [2] is correct as shown in Eq. (8):

$$C_{\mathrm{H}}^{D\sigma} < C_{\mathrm{H}}^{D} \tag{8}$$

Therefore, it is demonstrated that the crack tip concentration is less than the bulk concentration due to the stress. It is interesting to note that Eq. (7) is the same as the equations derived by the Dutton–Puls model shown in Eqs. (2) and (3) only if the bulk and crack tip solubilities are governed by the same solvi irrespective of how to approach the test temperature by cooling or by heating (more details are given in Eqs. (9)–(11) in Section 2.4).

The reason why Puls could not understand Eq. (8) seems to be related to his misconception that the chemical potential of the stressed region reaches zero at equilibrium or $\Delta\mu_{\mathrm{H}}^{\sigma>0} = 0$. The same misconception was applied to determine the concentration in the stressed region of the crystal: "*Equilibrium between the regions at zero stress and at arbitrary stress is obtained when the chemical potentials for diffusion are equal. This yields that at equilibrium the concentrations in the stressed part of the crystal is increased over that in the unstressed part*" [3]. However, at equilibrium, the chemical potentials of hydrogen are equal between the stressed and unstressed regions, causing no diffusion of hydrogen and hence no DHC. In other words, DHC stops as soon as the crack tip concentration increases above the bulk concentration. Thus, an increase of the concentration in the stressed region due to the stress corresponds to the condition for DHC arrest, not the condition for DHC initiation. Considering that Puls's claim that the concentrations in the stressed part are increased over that in the unstressed part disagrees with his analytical equations shown in Eqs. (1)–(3), it is demonstrated that Puls's claim is incorrect.

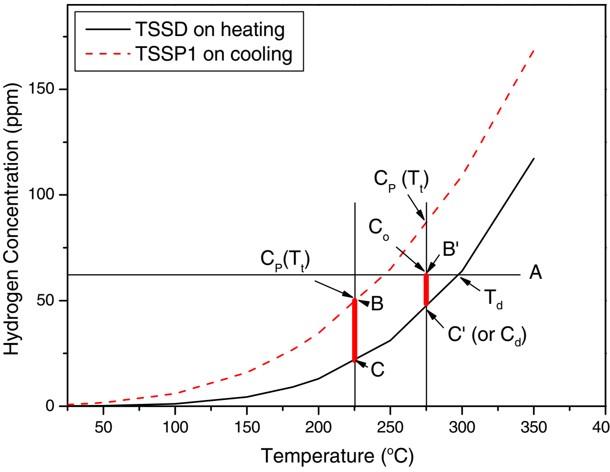

Fig. 1. The bulk and crack tip solubilities depending on the initial concentration of the specimen, C_o when compared to the cooling solvus at the test temperature $[C_P(T_t)]$. The driving force ΔC is either the distance B′C′ when C_o is less than $C_P(T_t)$ or the distance BC when vise versa, respectively.

2.4. Analytical expressions for the local hydrogen solubilities

One of the difficulties with deriving the analytical equations for the CGR is how to define the local hydrogen solubilities at the crack tip and in the bulk. According to the Dutton–Puls model, if the work term due to the stress or the hydride interaction energy [3] is disregarded during heating or cooling due to the absence of the stress, it is assumed that the bulk solubility and the crack tip solubility would be determined by the heating solvus C_{H}^{heat} (=TSSD) and the cooling solvus C_{H}^{cool} (=TSSP1), respectively, as shown in Eqs. (2) and (3), claiming that the bulk and crack tip follows the different solvi irrespective of how to approach the test temperature either by heating or by cooling. If this claim were true, then the bulk concentration and the crack tip concentration at 225 °C upon an approach by heating correspond to points C and B, respectively, as shown in Fig. 1, according to Eqs. (2) and (3). Note that point B (=crack tip concentration) is higher than point C (=the bulk concentration) at any test temperature approached by heating even without the stress, which is illogical. When the stress is applied only at the crack tip upon arrival at the test temperature, the crack tip concentration corresponding to point B in Fig. 1 will decrease according to Eq. (3) but cannot go below TSSD (=point C in Fig. 1) corresponding to the bulk concentration. Therefore, the concentration difference or ΔC between the bulk concentration and the crack tip would be negative or zero despite the stress being applied to the crack tip, indicating that no DHC would occur according Eqs. (1)–(3). Hence, it is demonstrated that the Dutton–Puls model shown in Eqs. (1)–(3) does not make sense.

In fact, since the stress is applied only upon arrival at the test temperature during the DHC tests, the work term applied by the stress can be disregarded on heating or cooling to the test temperature. In case of heating or cooling without the stress, the bulk and the crack tip should follow the same solvi rather than the different solvi depending on the position in zirconium alloys as assumed by the Dutton–Puls model [1,3]: either TSSD on heating (corresponding to point C at 225 °C in Fig. 1) or TSSP1 on cooling (corresponding to B at 225 °C on cooling from 320 °C in Fig. 1). However, if the initial hydrogen concentration, C_o (corresponding to point B′ in Fig. 1) is lower than the cooling solvus or $C_P(T_t)$ at 275° when approached by cooling from 320 °C as shown in Fig. 1, the hydrogen concentration in solution in the bulk and at a crack tip should be the same as C_o. Consequently, it is clear that the analytical equations for the local solubilities derived by the Dutton–Puls model described in Eqs. (2) and (3) should be revised as such:
on heating,

$$E_L = C_{\mathrm{H}}^{heat}\exp[\overline{w}_t^{a}(L)/RT] \cong C_{\mathrm{H}}^{heat}, \quad E_l = C_{\mathrm{H}}^{heat}\exp[\overline{w}_t^{a}(l)/RT] \cong C_{\mathrm{H}}^{heat} \tag{9}$$

on cooling when C_o is higher than C_{H}^{cool} at the test temperature

$$E_L = C_{\mathrm{H}}^{cool}\exp[\overline{w}_t^{a}(L)/RT], \quad E_l = C_{\mathrm{H}}^{cool}\exp[\overline{w}_t^{a}(l)/RT] \tag{10}$$

or on cooling when C_o is less than C_{H}^{cool} at the test temperature

$$E_L = C_o\exp[\overline{w}_t^{a}(L)/RT], \quad E_l = C_o\exp[\overline{w}_t^{a}(l)/RT] \tag{11}$$

In case of heating as shown in Eq. (9), the bulk solubility E_L and the crack tip solubility E_l should be the same as C_{H}^{heat} or TSSD because the heating solvus changes little with the stress [7,25], leading the ΔC to be zero. In other words, no DHC would occur on heating according to the Dutton–Puls model. Nevertheless, Puls predicted that DHC would occur even at high temperatures above 300 °C as shown in Fig. 1 in [2] in case of heating. It is unclear how DHC is predicted to be able to occur in Zr–2.5Nb tube at those high temperatures above 300 °C on heating according to the

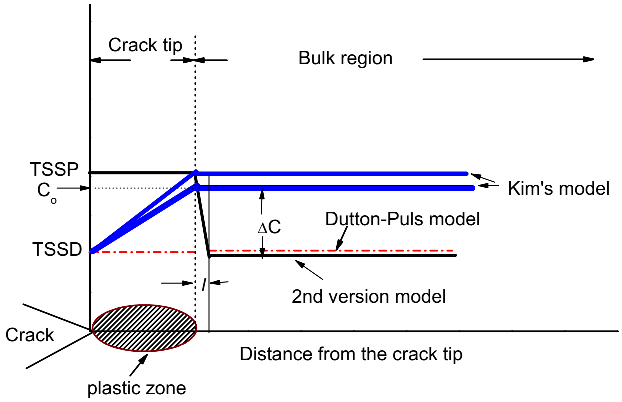

Fig. 2. Diagram showing the concentration gradient formed at the crack tip that differs with the DHC models: the crack tip concentration is the same as the heating solvus or TSSD according to Eqs. (3) and (9) of the Dutton–Puls model termed the 1st version model and Kim's model but the second version model claims that the crack tip concentration corresponds to the cooling solvus or TSSP. Note that although it is assumed according to Eq. (1) of the Dutton–Puls model that the bulk concentration is higher than the crack tip concentration, Eq. (9) shows that the bulk concentration is the TSSD on heating, creating no concentration gradient between the bulk and the crack tip. l in Fig. 2 represents the size of the zone where the hydrogen concentration gradient is formed according to the old DHC models while the hydrogen concentration gradient is formed over the plastic zone according to Kim's model.

Dutton–Puls model. Furthermore, the fact that DHC at low temperatures below 180 °C occurs even on heating cannot be explained according to Eq. (9) predicting no DHC on heating. However, on cooling, as shown in Eqs. (10) and (11), the applied stress always decreases the crack tip solubility, E_l leading it to be lower than the bulk solubility E_L, creating the ΔC between the bulk and the crack tip that is the driving force for hydrogen to diffuse from the bulk to the crack tip. This physical concept is identical to Kim's model except Puls's misconception that the decrease in hydrogen concentration can occur without precipitation of hydrides due to the applied stress.

In short, to better explain the difference in the DHC models proposed so far, the concentration gradient at the crack tip is schematically described in Fig. 2. According to Eqs. (1)–(3), the Dutton–Puls model says that the crack tip concentration is reduced to the TSSD than the bulk concentration, which is the same as Kim's model, except a region where the concentration gradient is formed, and the bulk concentration. However, the so-called second version model [2] including McRae's model [7] and Shi's model [26] claims that the crack tip concentration is higher than the bulk concentration. In contrast, on cooling, the bulk concentration is either the initial hydrogen concentration C_o or the TSSP, according to Kim's model but on heating, it corresponds to the heating solvus or TSSD irrespective of the stress effect, according to Eq. (9) although Eqs. (1)–(3) of the original Dutton–Puls model assume that the bulk concentration is higher than the crack tip concentration. The author's analysis of the Dutton–Puls model exhibits that, as shown in Eq. (9), the crack tip and the bulk should have the same solvus as the heating solvus on heating, creating no concentration gradient, as shown in Fig. 2. Despite the second version model's claim [2,7,26] of the crack tip concentration that should increase to the TSSP1, however, their analytical equations for the CGR indicate that the bulk concentration is higher than the crack tip concentration [2,7], which disagrees with the concentration gradient illustrated in Fig. 2.

2.5. Stress effect on the CGR

Against the author's criticism [2] that the Dutton–Puls model cannot predict the experimental observation that the CGR is constant independent of K_I above $K_I > K_{IH}$, Puls [1] has conceded that this criticism is *correct due to the boundary conditions used in the Dutton–Puls model where all the hydrogen coming towards the crack tip from the bulk was chosen to come from the bulk hydrides that would be closest to the crack tip hydride. However, if one could choose the bulk hydride far away from the crack tip hydride as a source of hydrogen, Puls claimed that the CGR would not depend on K_I*. However, his claim [1] is unreasonable because the bulk hydride closest to the crack tip hydride must supply hydrogen most efficiently to the crack tip first of all in view of hydrogen diffusion if the bulk hydrides are the source of hydrogen which is one of the defects in the Dutton–Puls model. Furthermore, given the distance between striations ranging from a few to several tens of micrometers [9,14,20], corresponding to the critical hydride length, a choice of a longer distance than the striation spacing as the distance between the bulk and the crack tip is invalid.

As another rebuttal to the author's criticism [2] given above, Puls [1] has claimed that *the Dutton–Puls model is not faulty since 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*. As shown in Eq. (9) in Section 2.4, no DHC should occur on heating in zirconium alloys, according to the Dutton–Puls model, because the bulk and crack tip solubilities are the same as the heating solvus regardless of the hydride interaction energy. Furthermore, given Puls' claim [1] that K_I independence arises from the interaction energy term, he may assume that the ΔC is constant independent of the magnitude of the interaction energy term, resulting in the constant CGR independent of K_I. If this were true, the Dutton–Puls model may explain K_I independence of the CGR but cannot do the yield stress dependence of the CGR [12,27,28]. This occurs because ΔC is likewise constant independent of the magnitude of the interaction energy term despite a change of the hydride interaction energy with the yield stress. Note that irrespective of the magnitude of the hydride interaction energy, the maximum ΔC or the maximum difference between the bulk and crack tip solubilities is bounded by the cooling solvus minus the heating solvus (or TSSP1–TSSD), corresponding to the distance B′C′ at 275 °C or BC at 225 °C, as shown in Fig. 1. Thus, considering that the yields stress just affects the local solubilities at the crack tip and in the bulk [1], as shown in Eqs. (1)–(3), the yield stress effect or the stress effect should disappear when the ΔC exceeds the ΔC_{max} corresponding to TSSP1–TSSD as shown in Fig. 1. Hence, it is clear that the Dutton–Puls model is too defective to explain the dependences of the CGR on K_I or the yield stress in zirconium alloys.

2.6. Effect of the direction approaching the test temperature

Regarding the author's criticism [2] that the Dutton–Puls model cannot explain the DHC arrest temperature, Puls [1] has refuted it by saying that *Kim should have referred to the most-up-to date analysis, which was that given by Shi et al.* [26]. The reason the author [2] has referred to Ambler's result is that Puls [1] claimed that *the old model could explain DHC arrest by citing Ambler's work*. Note that using the Dutton–Puls model [2,3], Ambler [10] 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. Given that the ΔC is related to nucleation of hydrides [18,20], Puls's claim [3] 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. As strong evidence against Puls's claim, the author [2] referred to the results of Resta Levi and Puls [29] showing nucleated hydrides at the crack that have been arrested. In contrast, Puls [1] refuted the author's remark by saying that *a DHC test was intentionally stopped below the arrest temperature to observe the hydride distribution at the crack tip*. Given that a rapid drop of the CGR is immediately followed by DHC arrest, the presence of nucleated hydrides at the crack during a rapid drop of the CGR proves that nucleation of hydrides has nothing to do with a rapid drop of the CGR or DHC arrest. More evidence to prove the validity of the author's remark is found from Shi et al. [26] saying that "*it was experimentally observed and theoretically proved that DHC is not possible even when hydrides are present at flaw tips*."

Claiming that *DHC is possible up to ~150 °C when approaching the test temperature from below* [1] by citing Shi's results shown in Fig. 3, Puls seems to refute the author's criticism that the Dutton–Puls model cannot explain the DHC arrest temperature. However, this refute comes from Puls's misunderstanding of Shi's experiment [26] where the DHC initiation temperatures were determined on cooling, not on heating, depending on the hydrogen concentration changing from 7 to 86.2 ppm. Thus, the results in Fig. 3 showed that on cooling from higher temperatures above the TSSD, DHC initiation occurred at 150 °C at the low concentration of 7 ppm H and above 200 °C at and above 29 ppm. Hence, it is clear that the point A in Fig. 3 has nothing to do with the DHC arrest but is related to the DHC initiation temperature on cooling. Note that point A corresponds to the crossing of the predicted bulk concentrations or C_o that increases the crack tip concentration to the TSSP1 due to the stress effect, and the measured bulk concentration to initiate DHC. In other words, point A indicates that DHC occurred when the initial hydrogen concentration, C_o was equal to the heating solvus termed C^d at low temperatures below 180 °C. However, this analysis shown in Fig. 3 is inconsistent with Shi' model [26] *predicting the DHC arrest by equating C_o to C^d*, which is the critical defect of Shi's model. Furthermore, given the experimental facts [20,29,30] that the DHC arrest above 300 °C occurred despite C_o being much larger than C^d, it is evident that Shi's model [26] is too defective to explain the DHC arrest above 300 °C even on cooling. In fact, Puls's claim [1] that the DHC arrest is predicted to occur at 150 °C on heating using Shi's model is inconsistent with Ambler's experimental facts, showing that the DHC arrest temperature was not constant but changed with the cooling rate and the hydrogen concentration in solution at the peak temperature: either 180 or 150 °C for the furnace-cooled Zr–2.5Nb and above 250 °C for the water-quenched one.

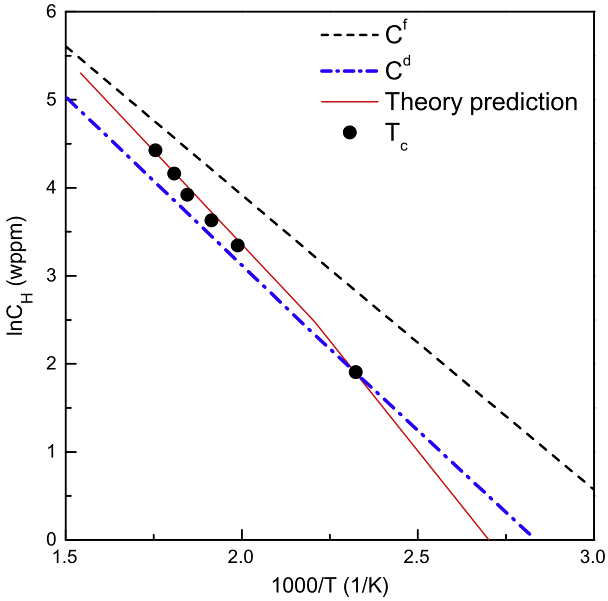

Fig. 3. Comparison of the measured DHC initiation temperature (or T_c) data on cooling from above with the heating solvus C^d, the cooling solvus C^f and the bulk concentration C_o.

3. Diffusion of hydrogen to the stressed region in a closed system

One of the assumptions of the old DHC models including the Dutton–Puls model [1,3–5] and the second version model [2,7,26] is that the stress can cause hydrogen to diffuse from the bulk to a crack tip regardless of how to approach the test temperature by heating or cooling. However, if this assumption were true, DHC should have occurred in zirconium alloys above 180 °C when approached by heating despite a large difference in the stress or the large stress gradient between the crack tip and the bulk. In fact, no DHC occurs above 180 °C irrespective of the magnitude of the stress difference unless the test temperature is approached by cooling [10,15], demonstrating that the role of the stress in hydrogen diffusion claimed by the old DHC models is questionable. Note that an increase in hydrogen concentration due to the stress difference or the stress gradient is known to be too small to reach the TSSP1 or the cooling solvus for hydride nucleation [2,3,7,31]. There is a real case demonstrating that the stress cannot cause the diffusion of hydrogen toward the stressed region: milk cannot come out of the milk carton 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 carton shrinks by pressing it with hands, then the milk comes out of it very easily. Likewise, since zirconium alloys with hydrogen in solution is a closed system, the stress applied to the crack tip cannot cause hydrogen to diffuse there from the bulk unless cooling is applied. It is well known that the hydride phase can be precipitated only by cooling a closed system [1,2,32]. As to the author's comment that zirconium alloys with hydrogen in solution is a closed system, Puls criticized that *it was another of Kim's misconceptions* although he admitted that *the closed system was closed to the external world*. Given that hydrogen cannot enter into or come out of zirconium alloys with hydrogen during deformation or cracking under the stress, zirconium alloys with hydrogen must be a closed system, demonstrating that it is Puls's misconception, not Kim's.

Since the chemical potential of hydrogen is reduced by the tensile stress, according to Eq. (6) in [2], the hydrogen solubility in the stressed region is theoretically reduced when compared to that in the unstressed region, as shown in Eqs. (2) and (3). Thus, the decrease of the hydrogen solubility in the stressed region may be possible thermodynamically due to the stress effect but cannot be done kinetically without the volume shrinkage that can replace a decrease in the volume of hydrogen in solution accompanied by precipitation of a hydride. Regarding the role of cooling, Puls [2] cast a doubt by saying that "*Kim believes the chemical potential for hydrogen in solution is affected by the decrease of the lattice spacing with decrease in temperature*." It seems that Puls [2] confuses thermodynamics with kinetics: thermodynamically, the lattice shrinkage by cooling has nothing to do with the chemical potential of hydrogen but kinetically squeezes hydrogen in solution in the unstressed region to easily move to the stressed region as with pressing the milk carton by hands. As already discussed above, without cooling, hydrogen cannot move to the stressed region from the unstressed region despite there being the chemical potential gradient for hydrogen between the stressed and unstressed regions due to stress. This is in contrast with the Dutton–Puls model [1,3–5] claiming that the stress always yields the concentration gradient, causing hydrogen to the stressed region from the unstressed region.

4. Kinetics of crack growth in zirconium alloys

DHC requires the three processes such as nucleation, growth and cracking of hydrides that should occur sequentially for a crack to grow in zirconium alloy [18,20]. Irrespective of the length of the time interval required to nucleate hydrides at the crack tip, the first step is nucleation of hydrides, which is the fact that cannot be denied. Furthermore, nucleation has nothing to do with diffusion [2]. Thus, the CGR is governed by the rate of the slowest process among the three processes. Hence, Puls's claim that DHC is governed solely by diffusion-controlled process or the rate of hydride growth is incorrect. Given that hydrides can be precipitated by cooling a closed system such as zirconium alloys [2,32], Puls's claim that diffusion of hydrogen is required to nucleate hydrides is another of Puls's misconceptions.

Note that nucleation of hydrides occur only under hydrogen supersaturation or ΔC that is created by cooling. The supersaturation of hydrogen represents the hydrogen concentration above the heating solvus that is dissolved in zirconium alloys. Unlike Puls's claim [1], the hydrogen supersaturation does not have to be equal to the difference between the nucleation solvus and the dissolution solvus despite the latter corresponding to the maximum supersaturation of hydrogen. Against the author' remark [2], Puls [1] claimed that "*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 approached from below according to this model. We have shown in Section 2.4 that this claim of Kim's is incorrect*." It is important to note that Puls's claim that Kim's claim is incorrect is Puls's misunderstanding, as already described in Sections 2.3–2.5 in this work. Besides, there are a great number of experimental facts [10,15] denying Puls's claim: DHC cannot occur above 180 °C irrespective of the magnitude of stress in zirconium alloys with hydrogen on approach the test temperature by heating as shown in Fig. 3 in [2]. Another of the experimental facts is no DHC at the TSSD temperature above 180 °C when the Zr–2.5Nb specimens were cooled from above to below the TSSD temperature corresponding to the TSSD or C_H^{heat}, as shown in Fig. 4. In other words, DHC did not occur when the bulk concentration in solution decreased to C_H^{heat} or TSSD on cooling to the TSSD temperature above 180 °C, but it occurred when the bulk concentration had a supersaturation of hydrogen by cooling below the TSSD temperature, as shown in Fig. 4. This fact shows that when the bulk concentration reaches C_H^{heat} upon arrival at the TSSD temperature on cooling, despite the stress effect increasing the crack tip concentration, the crack tip concentration cannot reach the cooling solvus or TSSP1, which is a necessary condition for DHC according to the Dutton–Puls model. Consequently, as evidenced by the experimental facts, Puls's claim that the crack tip solubility can increase to the TSSP1 by a stress-assisted diffusional increase of hydrogen when the test temperature approached from below is incorrect.

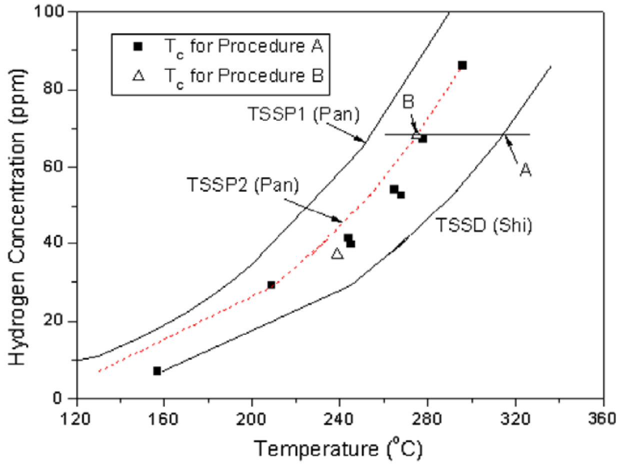

Fig. 4. DHC initiation temperatures with hydrogen concentration for a Zr–2.5Nb tube, which were determined only after the first thermal cycle where the specimens were cooled stepwise under the stress from 20 °C above the TSSD temperature: note that DHC was seen to occur at lower temperatures than the TSSD temperatures above 180 °C and just at the TSSD temperature below 180 °C.

Regarding Puls's assertion [1] that *the mechanism of stress-assisted δ-hydride formation at the crack tip proposed by Kim is not credible*, it should be noted that the formation of δ-hydrides at the crack tip is the experimental fact that cannot be denied as shown in Fig. 8 in [2]. Furthermore, according to Root's experimental fact [33] (Fig. 11 in [2]) and Khatamian's observation [34], it is the γ-hydride, not the δ-hydride that is stable in the bulk at as low a temperature as 50 °C. Thus, the experimental fact is that the δ-hydride is precipitated at the crack tip and the γ-hydride is formed due to the stress-induced transformation from δ to γ, which is the core of the author's low temperature DHC model. It is evident that Puls's criticism [1] on the author's remark, which was made *assuming that hydride nucleation and growth is governed by TSSP1*, is totally incorrect.

5. Conclusions

This work has shown that Kim's criticism that the Dutton–Puls model for the CGR is established based on a faulty thermodynamic basis is correct. The old DHC models including the Dutton–Puls model termed the first version model and the second version model show that the CGR is governed by the ΔC, not the stress gradient, demonstrating that Puls's claim that the stress gradient is the driving force for the DHC is incorrect. The analytical equations of the Dutton–Puls model show that the crack tip solubility is always lower than not only the bulk solubility but also the cooling solvus or TSSP1 whenever the stress is applied only at the crack, demonstrating that Puls' claim that the crack tip solubility should increase to the TSSP1 for hydride precipitation is inconsistent with the Dutton–Puls model. In fact, the author's analysis of the Dutton–Puls model shows that no DHC is predicted to occur on heating. Another of Puls's misconceptions is that hydrogen can diffuse to the stressed region from the unstressed region in zirconium alloys that are a closed system. In the closed system, hydrides cannot be precipitated without cooling irrespective of the magnitude of the stress without the hydride phase transformation from γ to δ, which is evidenced by the experimental facts. Given the fact that DHC involves the three processes such as nucleation, growth and cracking of hydrides at the crack tip, the CGR should be governed kinetically by the rate of the slowest processes among them, which is the core of Kim's model. Hence, Puls's claim that DHC is simply a diffusion-controlled process and the CGR is governed solely by the rate of hydride growth is incorrect, yielding many of the unsolved issues related to DHC. The strongest point is that Kim's model can explain all of the DHC issues that remain unresolved to date.

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