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Letter to the Editor

Comment on ‘The first step for delayed hydride cracking in zirconium alloys’ by G.A. McRae et al., J. Nucl. Mater. 396 (2010) 130–143

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ABSTRACT

The aim of this paper is a reply to McRae et al.’s paper entitled “The first step for delayed hydride cracking (DHC) in zirconium alloys” claiming that the first step of DHC is hydrogen diffusion, not nucleation of hydrides as demonstrated by Kim’s new model. Despite the authors’ claim that the crack tip concentration is higher than the bulk concentration due to the stress gradient, their claim violates the thermodynamic principle that the stressed region should have a lower potential of hydrogen or lower hydrogen solubility than the unstressed region. Furthermore, it is demonstrated that the Diffusion First Model (DFM) proposed by the author is defective in terms of kinetics because hydrogen diffusion before hydride nucleation just governs the rate of hydride nucleation, neither the rate of hydride growth nor the crack growth rate (CGR).

1. Introduction

McRae et al. [1] submitted a paper entitled “The first step for delayed hydride cracking (DHC) in zirconium alloys” claiming that the first step of DHC is hydrogen diffusion, not nucleation of hydrides as demonstrated by Kim’s new model [2–7]. They have claimed that the driving force for hydrogen diffusion is the stress gradient and the crack growth rate (CGR) or DHC rate is governed only by hydrogen diffusion. However, they have not considered the effect of nucleation and cracking of hydrides on the CGR of zirconium alloys. Thus, as the first process of DHC is claimed to be hydrogen diffusion from the bulk to a crack tip under high tensile stresses, they have claimed that they are the first one to suggest the so-called Diffusion First Model (DFM) when compared to the models suggested by Dutton and Puls [8,9] and by Shi et al. [10]. Given both the authors’ model and the latter’s models assuming that hydrogen diffusion is the first process of DHC, however, the authors’ claim is arbitrary and unreasonable. Furthermore, they have claimed that Dutton and Puls’s model assumes precipitation of hydrides to be the first process of DHC, termed the Precipitation First Model (PFM), and thus, Kim’s model is just the extension of Dutton and Puls’s PFM model [1]. Note that no explicit words saying that precipitation of hydrides is the first process of DHC have been given in any of Puls’s papers [8,9,11–13]. Nevertheless, accounting for Dutton and Puls’ assumption that the crack tip solubility is lowered by stresses, the authors have simply asserted that lowering the hydrogen concentration in solution at a crack tip occurs only after precipitation of hydrides, leading them to call Dutton and Puls’s model [8,9] the PFM. However, they should have understood the assumptions of Dutton and Puls’s model [8,9] that result in lowering the crack tip solubility: the molar volume of hydrogen was assumed to be different between zirconium and hydride, which would cause the crack tip solubility to decrease due to the stress even without any precipitation of hydrides [8,9]. As it is later known that the molar volume of hydrogen is the same between zirconium and hydride [14], however, the crack tip solubility cannot be lowered due to the stress without precipitation of hydrides. This is the idea of Kim’s model [2–7] that has been proposed for the first time. No one but Kim has come up with this new idea that precipitation of hydrides is the first step, resulting in the difference in hydrogen concentration between the bulk and a crack tip. Nevertheless, they went too far by claiming that Dutton and Puls’s model was the PFM and Kim’s model was not new but an extension of Dutton and Puls’s model.

The aim of this work is to demonstrate that the first step of DHC is nucleation of hydrides, not hydrogen diffusion as claimed by McRae et al. and the CGR is governed not simply by hydrogen diffusion but by the rate of the slowest processes among the three consecutive processes involved in DHC: nucleation, growth and cracking of hydrides. Consequently, this work shows the validity of Kim’s model [2–7].

2. Understanding of DHC processes

According to Cann and Sexton’s experiment [15], hydrides nucleated at a notch tip even at room temperature, grew to a

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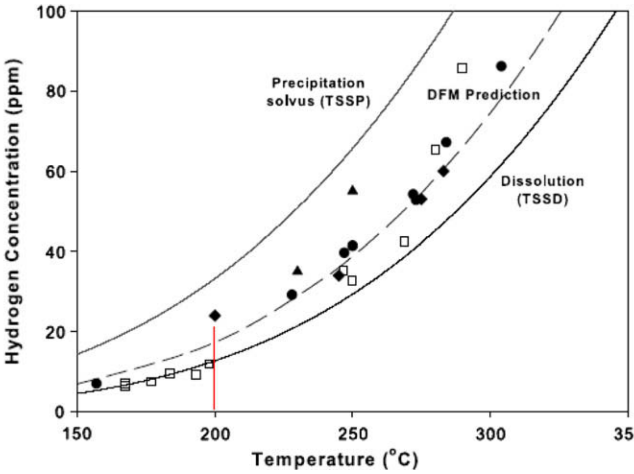

Fig. 1. Comparison of the DFM prediction lines (dotted lines) with the measured DHC initiation temperatures (symbols), showing that below 200 °C, the DFM prediction lines deviate from the measured ones.

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. 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 [16], 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. 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 [5,17]. 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. However, DHC below 180 °C cannot be explained by the DFM model proposed by the authors because the latter has assumed that DHC would occur only when the crack tip concentration reaches the TSSP. Evidence is found from Fig. 1 [1] demonstrating that the predicted DHC initiation temperature by the DFM is always lower than the TSSD temperature despite the fact that DHC initiation has occurred at the TSSD temperature at low temperatures below 200 °C (below the red[1] line). This is the critical defect of the DFM.

3. Comment on the Diffusion First Model (DFM)

3.1. Rate-determining process for crack growth rate (or DHC rate)

Given that DHC consists of the three consecutive processes such as nucleation, growth and cracking of hydrides [18], it is not really important which process is the first one between hydrogen diffusion and precipitation of hydrides or nucleation of hydrides. Despite the DFM where hydrogen diffusion is the first process of DHC, hydrides should nucleate at a crack tip and grow to a certain critical length followed by cracking to cause a crack to grow by DHC. The so-called DFM model proposed by the authors have just asserted that diffusion of hydrogen increasing the crack tip concentration to the TSSP is the rate-controlling process, assuming that nucleation, growth and cracking of hydrides involved in DHC would be faster than the former. However, as the rate of hydrogen diffusion before nucleation of hydrides just affects the rate of hydride nucleation, not the hydride growth rate, the DFM's claim would be as if the hydride nucleation rate would govern the CGR. Given that nucleation of hydrides is so fast due to the large hydrogen supersaturation and tensile stress states at a crack tip [19], the governing process for the CGR is the rate of hydride growth, not the rate of hydride nucleation. This can explain why the CGR has a positive temperature dependence below 300 °C [18]. Unless the supersaturation of hydrogen is lower than the critical value corresponding to the hysteresis of hydrogen solubility at any temperature [19], then the rate of hydrogen diffusion before nucleation of hydrides would not affect the CGR at all. In other words, in case that hydrogen diffusion is the slowest process among them, it is the rate of hydrogen diffusion after nucleation of hydrides, not before it, that governs the CGR. Thus, the DFM model claiming that the rate of hydrogen diffusion before hydride nucleation governs the CGR is faulty.

3.2. The role of stresses

As the DFM claims that the first step is hydrogen diffusion from the bulk to a crack tip under the stress gradient, the hydrogen concentration in the stressed region is higher than that in the unstressed region as shown in Eq. (18) [1]. The same claims were proposed also by Shi et al. [10] and very recently by Puls [20]. However, these claims must be feasible only in an open system, not in such a closed system as the Zr–H system where hydrogen dissolved in zirconium cannot move from the bulk to a crack tip under the stress gradient, were it not for the concentration gradient. An analogy is that milk in the milk box cannot come out of it unless it shrinks although a pumping force is applied though a straw inserted in it. Furthermore, they violate the thermodynamic principle that the chemical potential of hydrogen in the stressed region is lowered than that in the unstressed region by $\sigma V_{\mathrm{H}}^{h}$ as shown in Eqs. (1) and (19) [1]:

$$\Delta\mu_{\mathrm{H}}^{\sigma>0} = \Delta\mu_{\mathrm{H}}^{0} - \sigma V_{\mathrm{H}}^{h}, \tag{1}$$

where $\Delta\mu_{\mathrm{H}}^{\sigma>0}$ is the chemical potential in the stressed region under the tensile stress of σ, $\Delta\mu_{\mathrm{H}}^{0}$ is the chemical potential in the unstressed region under zero stress, V_{H}^{h} is the increased volume due to precipitation of a hydride. It should be noted that the hydrogen solubility is determined by the chemical potential of hydrogen as shown in:

$$\Delta\mu_{\mathrm{H}}^{0} = \mu_{\mathrm{H}}^{D} - \mu_{\mathrm{H}}^{0} = RT\ln C_{\mathrm{H}}^{D}, \tag{2}$$

where μ_{H}^{0} is the chemical potential at the reference level, C_{H}^{D} is the diffusible hydrogen concentration and R and T have their usual meaning. As the applied stress has an effect on the decrease in chemical potential of hydrogen in the stressed region as shown in Eq. (1), thus reducing the hydrogen solubility in the stressed region, the stressed region must have a lower hydrogen concentration in solution than the unstressed region as shown in:

$$C_{\mathrm{H}}^{D} \text{ at a crack tip} < C_{\mathrm{H}}^{D} \text{ in the bulk}. \tag{3}$$

Against this comment, however, the authors have claimed that the terminal solid solubility for hydride precipitation (TSSP) corresponding to the crack tip solubility does not change with stresses. Nevertheless, the authors showed that the crack tip hydrogen concentration in solution was calculated to increase due to the stress

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[1] For interpretation of color in Figs. 1–4, the reader is referred to the web version of this article.

effect as shown in Fig. 6 [1]. Given that the concentration of hydrogen in solution corresponds to the hydrogen solubility, it should be kept in mind that the increased crack tip concentration represents the increased crack tip solubility due to the stress effect. Hence, it is clear that the increased crack tip concentration due to the stress is inconsistent with the author's claim that the TSSP does not change with stresses.

Although there is a thermodynamic driving force that the stress decreases the chemical potential as shown in Eq. (1), this cannot occur kinetically without precipitation of hydrides in the stress region. To incur precipitation of the hydrides, the supersaturation of hydrogen is required, which can be obtained using a thermal cycle that is a necessary condition for DHC to occur above 180 °C. In other words, in isothermal conditions without any cooling, the stress applied to the crack tip cannot cause the hydride to precipitate due to no hydrogen supersaturation, leading to no change in the crack tip concentration. Experimental evidence is provided by Simpson and Nuttal [21] who have shown 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.

3.3. Crack growth rate (CGR) equation

Despite the authors' claim that the crack tip should have a higher concentration when compared to the bulk (Eq. (12) [1]), the CGR (or crack velocity) equation derived by them shows the opposite result, as shown in Eq. (17) [1]. If the activity coefficient γ of hydrogen is assumed to be the unity irrespective of the position, then the crack growth rate V in Eq. (17) [1] is simply expressed as

$$V = \frac{k(T)2\pi D}{\Phi}\left(C(b)\exp\left[\frac{\mu^0(b)-\mu^0(a)}{RT}\right] - C(a)\right), \tag{4}$$

where $C(b)$, $\mu^0(b)$, $C(a)$ and $\mu^{0}(a)$ denote the hydrogen concentrations and chemical potentials at $r = b$ and at $r = a$, respectively and the other symbols have the same meaning as in [1]. Considering diffusion of hydrogen from the bulk or $r = b$ to the crack or $r = a$, as shown in Fig. 4 [1], it is clear that the $C(b)$ and the $C(a)$ represent the bulk hydrogen concentration and the crack tip concentration, respectively. Thus, Eq. (4) shows that the bulk concentration is higher than the crack tip concentration, which is in contradiction with the author's claim that the crack tip concentration is higher than the bulk concentration, as shown in Eq. (12) [1]. Note that the physical significance of Eq. (4) (shown above) demonstrates that the stress gradient operating only at a crack tip does not change the crack tip concentration but does affect the bulk concentration with no stress gradient, which is unreasonable. Consequently, it is clear that Eq. (4) or Eq. (17) [1] derived by the author is inconsistent, demonstrating that the DFM proposed by the author is not valid. As the bracket in Eq. (4) represents a difference in the hydrogen concentration between the bulk and the crack tip, or ΔC, thus, Eq. (4) can be rewritten as

$$V = \frac{k(T)2\pi D}{\Phi}\Delta C \tag{5}$$

Thus, the CGR is governed by the supersaturation of hydrogen or ΔC, demonstrating the validity of Kim's model that the ΔC is the driving force for DHC. Given that Φ and $k(T)$ are the constants, it is clear that the CGR equation (Eq. (5)) derived by the authors is too simple to contain variables such as the threshold stress intensity factor or K_{IH}, the yield strength and the critical hydride length. Furthermore, without a constant $k(T)$ [1] that has been introduced without any rationale, the activation energy for the CGR should have been the same as the activation energy for hydrogen diffusion, according to Eq. (5). Nevertheless, the authors have claimed that the DFM predicts the apparent activation energy for DHC of $Q = 47$ kJ/mol [1] which is larger than the activation energy for hydrogen diffusion. However, as shown in Eq. (5), the DFM cannot explain the physical significance of $Q = 47$ kJ/mol. It should be noted that if the CGR is governed by the total hydrogen flux, the CGR should be expressed as

$$V = -kJ_{\mathrm{H}} = kD\frac{\Delta C}{\Delta X} \tag{6}$$

where D is the diffusivity of hydrogen, and $\Delta C/\Delta X$ is the concentration gradient. As Eq. (5) in this study or Eq. (17) [1] excludes ΔX, it is clear that the governing equation for the crack growth rate derived by the authors is defective.

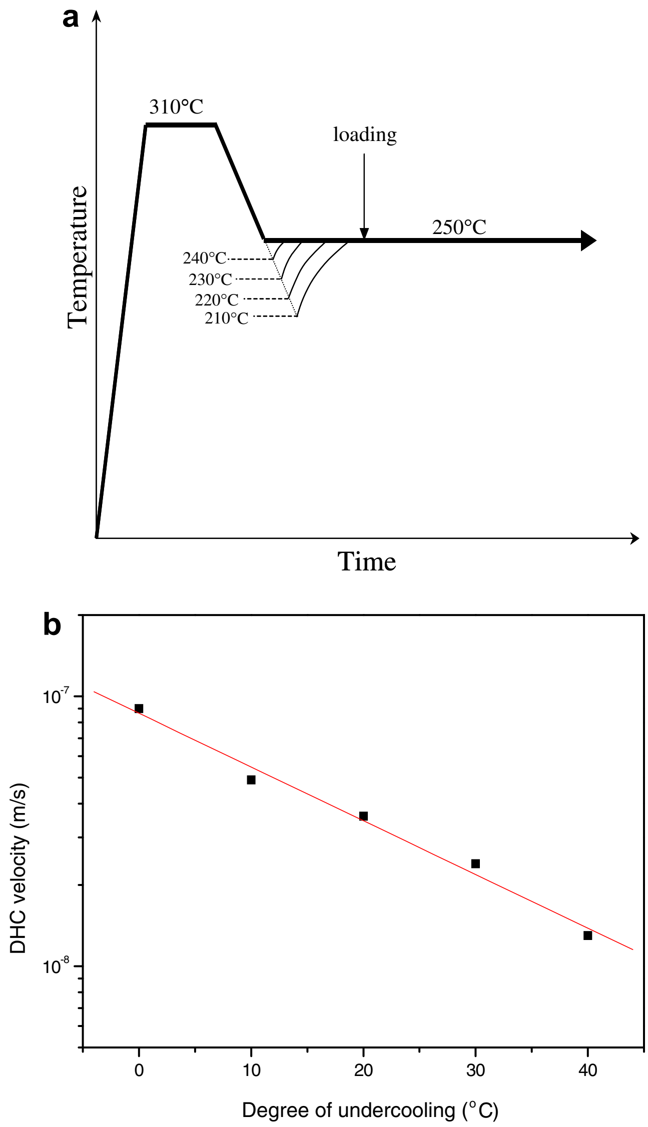

Fig. 2. (a) Thermal cycles applied for the undercooling experiment where the Zr–2.5Nb specimens with 60 ppm H were undercooled from 210 to 250 °C before approaching the test temperature of 250 °C from 310 °C. (b) DHC velocity (or crack growth rate) of the Zr–2.5Nb with the degree of undercooling before reaching the test temperature of 250 °C.

3.4. Effect of undercooling on the CGR according to the DFM

Through the so-called undercooling experiment where the cold-worked Zr–2.5Nb specimens with 60 ppm of hydrogen were heated to 310 °C, cooled to 250, 240, 230, 220 and 210 °C,

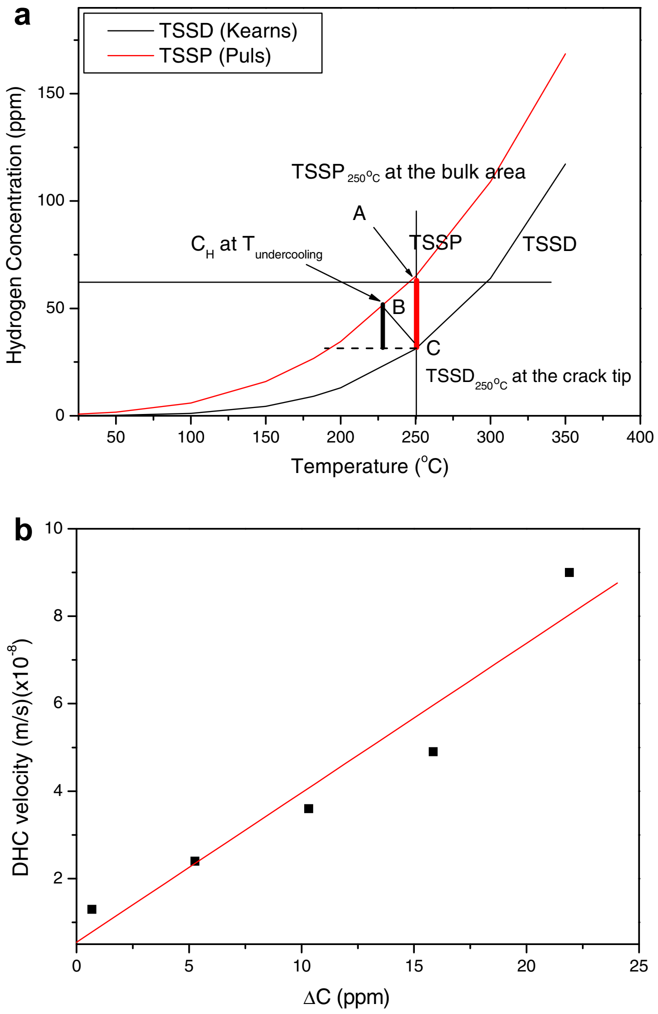

Fig. 3. (a) Diagram illustrating how the ΔC between the bulk and a crack tip is determined by the undercooling temperature where the crack tip concentration is fixed as the TSSD at the test temperature of 250 °C and the bulk concentration is reduced to the TSSP depending on the undercooling temperature. (b) Shows the DHC velocity (crack growth rate) of the Zr–2.5Nb with the supersaturation of hydrogen or ΔC.

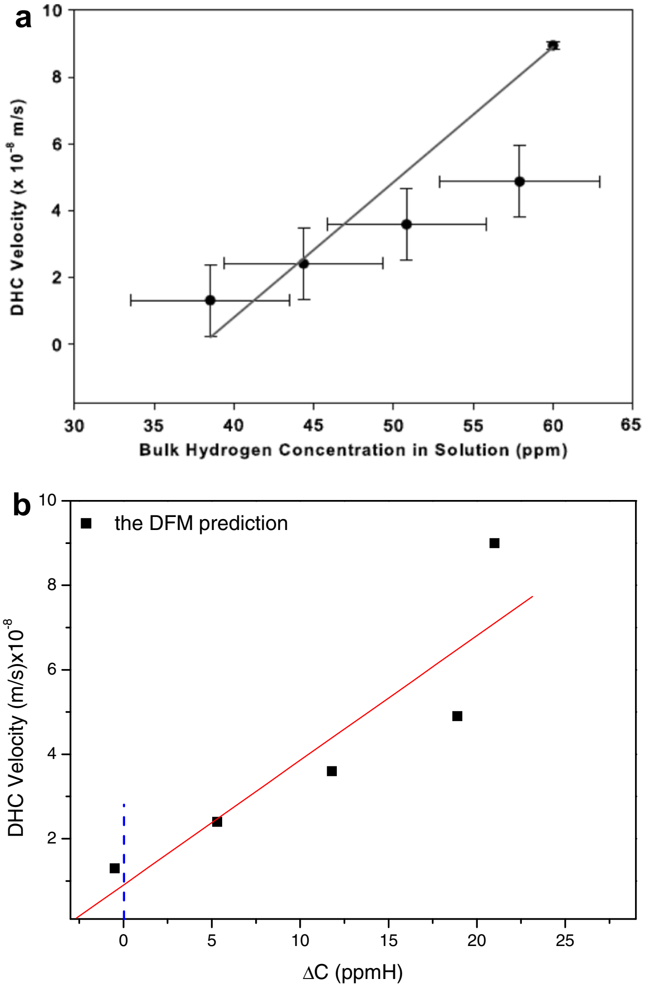

Fig. 4. (a) DHC velocity (crack growth rate) with the total hydrogen concentration in solution according to the DFM proposed by McRae [1] and (b) plotting the DHC velocity (crack growth rate) with the ΔC according to Eq. (24) [1], showing that the ΔC becomes negative when undercooled to 210 °C showing that the bulk concentration becomes lower than the crack tip concentration, which is unrealistic.

respectively, and then heated up to the fixed test temperature of 250 °C as shown in Fig. 2a [2], Kim et al. showed that the CGR was reduced to 1.3×10^{-8} m/s upon undercooling to 210 °C before reaching 250 °C and was increased to 9×10^{-8} m/s with no undercooling, as shown in Fig. 2b. Given that the crack tip concentration is reduced to the TSSD at 250 °C due to the stress effect irrespective of the degree of undercooling and the bulk concentration corresponds with the TSSP at the temperature to which the specimens has been cooled before heating up to the test temperature, the ΔC was determined to correspond to the distance BC of Fig. 3a, depending on the undercooling temperatures [2]. When the CGR was plotted as a linear function of the ΔC, as shown in Fig. 3b, it was found that the CGR was increased with the ΔC as shown in Fig. 3b.

The authors have claimed that the DFM can explain the results of our undercooling experiment by plotting the CGR with the bulk hydrogen concentration as shown in Fig. 4a, which is hard to understand. Given that according to the DFM, the CGR linearly depends on the ΔC as with both Eq. (5) in this study and Eq. (24) [1], the CGR should have been plotted with the ΔC as shown in Fig. 4b, not with the bulk hydrogen concentration (Fig. 4a). However, when the ΔC was calculated using Eq. (24) [1], the ΔC was found to be negative especially when undercooled to 210 °C, as shown in Fig. 4b, demonstrating that the bulk concentration is lower than the crack tip concentration. Under this situation with no driving force for hydrogen to move from the bulk to the crack tip, no DHC would occur when undercooled to 210 °C. In other words, the DFM could predict no DHC at 210 °C, strongly demonstrating that the DFM is a defective model. Regarding the crack tip concentration, Puls has assumed that it would be lowered to the heating solvus or TSSD [22,23]. Kim's model also demonstrates that it is reduced to the TSSD [2–7]. However, by claiming that the TSSP would not change with stresses, the authors insist that the crack tip solubility would correspond to the TSSP, not to the TSSD [1]. Nevertheless, according to Eq. (24) [1] and Eq. (5) in this study, the DFM predicts that the crack tip concentration would be 39 ppm at 250 °C, which is much lower than the TSSP. This fact shows that the authors' claim that the crack tip solubility should correspond to the TSSP is inconsistent with Eq. (24) [1] derived by the DFM. Considering that the TSSD at 250 °C is around 31 ppm H, it cannot be explained reasonably why the crack tip concentration calculated by the DFM is above the TSSD but below the TSSP despite the authors' claim that the crack tip should have the TSSP.

3.5. High temperature DHC limit according to the DFM

According to Eqs. (24) and (37) [1], the CGR should increase with increasing temperature. In other words, the DFM derived by the authors contains no variables related to the high temperature DHC limit which is the basic defect of the DFM. It should be noted that as shown in Eqs. (24) and (37) [1], hydrogen always moves from the bulk to the crack tip under the driving force of the ΔC regardless of temperature. Nevertheless, the authors hypothesize that at the higher temperature, equilibrium is reached so the flux goes to zero, leading to no cracking. However, this hypothesis disagrees with Eqs. (24) and (37) [1] predicting a hydrogen flux from the bulk to the crack tip independent of the test temperature. Furthermore, as the DFM does not have a variable related to K_{IH} (Eqs. (24) and (37) [1]), the authors cannot have any rationale to explain the effect of K_{IH} on the CGR. As they have disregarded the effect of hydride cracking on the CGR in establishing the DFM, it is natural that the DFM cannot explain a DHC arrest or the high temperature DHC limit above 300 °C. It should be noted that the high temperature limit is associated with a rapid increase of K_{IH} or the steep rise of hydride cracking resistance indicating that the hydride cracking rate becomes a rate-determining process for the CGR [18]. Hence, it is clear that the DFM is too defective to explain no DHC at high temperatures above 300 °C. Furthermore, the authors seemed to be confused about the effects of no hydrogen flux and a sharp increase of K_{IH} on the high temperature DHC limit. If no hydrogen flux were the cause of the DHC arrest, this assumption indicates that nucleation of hydrides is the governing process because it is determined by the ΔC. On the other hand, if the sharp increase of K_{IH} were the cause, then this assumption indicates that the cracking of hydrides is the governing process because K_{IH} determined the cracking resistance of hydrides. Given that hydrides can nucleate above 300 °C [21], the absence of hydrogen flux should not be the cause of the high temperature DHC limit.

4. Conclusions

The authors have proposed the Diffusion First Model (DFM) assuming that hydrogen diffusion is the first process of DHC, leading the hydrogen concentration in solution at a crack tip to become greater than that in the bulk due to the stress gradient. A big assumption of the DFM is that hydrogen can move to the crack tip due to the stress, which is impossible to occur in a closed system such as the Zr–H system. Furthermore, the DFM's hypothesis assuming the higher crack tip solubility than the bulk solubility violates the thermodynamic principle that applied stresses lower the chemical potential of hydrogen or the hydrogen concentration in solution at the crack tip when compared to that in the bulk. Nevertheless, the governing equation for the CGR has shown the crack tip concentration to be lower than the bulk concentration due to the applied stress effect, which is inconsistent with the DFM's hypothesis. The authors' CGR formula demonstrating that the CGR is determined by the ΔC is almost the same as that of Dutton and Puls except the crack tip concentration: the latter has assumed it to be reduced to the TSSD while the former assumes it to be above the TSSD for which no physical rationale has been given. Due to this assumption of the crack tip concentration being above the TSSD, the DFM cannot satisfactorily explain the results of Kim's undercooling experiment because the ΔC turns out to be negative when undercooled to 210 °C. The most critical defect of the DFM is to assume that diffusion of hydrogen increasing the crack tip concentration to the TSSP is the rate-controlling process, implying that nucleation, growth and cracking of hydrides involved in DHC would be faster than the former. As the rate of hydrogen diffusion before nucleation of hydrides just affects the rate of hydride nucleation only, the DFM model claiming that the rate of hydrogen diffusion before hydride nucleation affects the CGR is faulty and unreasonable if the CGR is governed by the other two processes than the hydride nucleation rate.

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