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Comment on ‘Influence of metallurgical variables on delayed hydride cracking in Zr–Nb pressure tubes’ by P. Cirimello et al., J. Nucl. Mater. 350 (2006) 135–146

Young S. Kim *

Korea Atomic Energy Research Institute, 150, Dukjin-dong, Yuseong, Daejeon 305-353, Republic of Korea

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Abstract

Reanalysis of the DHC initiation temperature, T_c and the crack propagation rate, V_p of CANDU and RBMK Zr–2.5Nb tubes, recently published by Cirimello et al., was conducted, using Kim’s DHC model. It is shown that a negative temperature dependency of V_p at above $T(\max V_p)$ for both Zr–2.5Nb tubes is due to a decreased hydrogen supersaturation below $\Delta C_{\min}$ over which V_p becomes independent of hydrogen concentrations. When compared to more than 200 data of V_p for the same Zr–2.5Nb tubes collected through the IAEA round robin tests, it is concluded that the temperature dependencies of their V_p which the authors determined using a single specimens are faulty.

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1. Introduction

In a recent paper by Cirimello et al. [1], the authors determined the delayed hydride cracking (DHC) initiation temperatures, T_c of CANDU and RBMK Zr–2.5Nb tubes with hydrogen concentrations and their crack propagation rate, V_p and discussed T_c and the temperature dependencies of their V_p using the previous DHC models suggested by Shi [2] and Puls [3], respectively. In predicting V_p, it was assumed that the cooling solvus or $C^S(l,L)$ at the crack tip and in the bulk would be different: TSSP1 (terminal solid solubility for precipitation) at the crack tip and TSSP2 in the bulk. Here, TSSP1 is the cooling solvus of the Zr–2.5Nb on a cooling from 420 to 450 °C while TSSP2 the one on a cooling from 220 to 368 °C [1]. Despite the experimental fact that T_c was higher than TSSP2 at all the hydrogen concentration, their assumption that the cooling solvus at the crack tip would reach TSSP1 is irrational. Moreover, the authors should have used one DHC model rather than two different models to account for V_p and T_c for the Zr–2.5Nb tubes. It should be noted that Shi’s model assumed a crack tip with a higher hydrogen concentration but Puls’s model supposed that the crack tip would have a lower hydrogen concentration when compared to the bulk despite the same hypothesis that the stress gradient is the driving force for DHC. In addition, the predicted V_p at above $T(\max V_p)$ by Puls’s model showed poor agreement with the measured V_p. Recently, we have proposed a new DHC model where the driving force for DHC is the concentration gradient arising from the stress-induced precipitation of hydrides at the crack tip, not the stress gradient [4–6]. Thus, I would like to comment and reanalyze the authors’ results with our new DHC model, which is the aim of this communication.

2. Comments

The authors suggested an equation for V_p based on Puls’s work such as

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* Tel.: +82 42 868 2359; fax: +82 42 868 8346.
E-mail address: yskim1@kaeri.re.kr

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$$V_{\mathrm{p}} = 2\pi D(E(L) - E(l))/[\Omega_{\mathrm{Zr}}\phi(L,l)t_{\mathrm{hyd}}N_{\mathrm{H}}x], \quad (1)$$

$$E(L,l) = C^{\mathrm{S}}(L,l)\exp\{\overline{W}_t^a(L,l) + p(L,l)\overline{V}_{\mathrm{H}}\}, \quad (2)$$

where $E(L,l)$ is the solubility of hydrogen in the bulk and at the crack tip, C^{S} the cooling solubility of hydrogen without stresses, $\overline{W}_t^a(L,l)$ the total interaction energy per mole of hydrogen due to hydride formation, $p(L,l)\overline{V}_{\mathrm{H}}$ the interaction energy of hydrogen in solution, t_{hyd} the hydride thickness and the other parameters are described in [1]. It should be noted that $E(L) - E(l)$ is equal to a hydrogen concentration difference or ΔC, implying that the bulk has a higher hydrogen concentration than the crack tip. In other words, Eq. (1) suggests that $E(L) - E(l)$ is the driving force for a hydrogen transfer from the bulk to the crack tip. This concept is very similar to Kim's DHC model [4–6] demonstrating that the ΔC is the driving force for DHC. However, a different point is that the hydrogen concentration gradient at the crack tip affecting V_{p} is not explicitly considered in Eq. (1) but it is so in Kim's DHC model [4–6]. Instead, Eq. (1) may involve the hydride thickness as a distance which is as small as 1–1.5 μm, but the hydride thickness, in fact, is not the plastic zone where the ΔC is formed. This accounts for a big increase of V_{p} with a slight change of the hydride thickness from 1.5 to 1.0 μm, as shown in Fig. 10a [1]. Accounting for the striation spacing that actually corresponds to the plastic zone formed ahead of the crack tip, ranging from 7 to 20 μm for a CANDU Zr–2.5Nb tube [7], an insertion of the striation spacing instead of the hydride thickness as small as 1.5 μm in Eq. (1) would result in at maximum 20 times decrease in the predicted V_{p}.

For C^{S} in Eq. (2), the authors assumed different cooling solvus between the crack tip and the bulk: TSSP1 and 0.9 TSSP1 at the crack tips of the CANDU and RBMK tube, respectively, and TSSP2 in the bulk of both tubes. However, this assumption is illogical because the cooling solubility of hydrogen without stresses should be the same regardless of the location in the sample and the tube type. To establish if the crack tip has TSSP1, the measured T_{c}'s for the Zr–2.5Nb tubes reported by the authors along with Shi's data were plotted against TSSD and TSSP2 lines as shown in Fig. 1. TSSD and TSSP lines involving TSSP1 and TSSP2 are drawn based on Kearns [8] and Pan [9], respectively. It should be noted that since T_{c} changed little with the number of cycles, the T_{c} data determined at the 1st cycle only is given in Fig. 1. The measured T_{c} data for both tubes by the authors were found to be much higher than TSSP1 and rather closer to TSSD. Therefore, the authors' assumption that the cooling solvus at the crack tip is TSSP1 is groundless. One thing to note is that the T_{c}'s of the CANDU Zr–2.5Nb tube by the authors are generally higher than the measured ones by Shi [2] at all the hydrogen concentrations. However, the authors gave no clear explanations for this difference in T_{c} despite the similar CANDU Zr–2.5Nb tubes being used by themselves and Shi [2]. The measured T_{c}'s of a RBMK Zr–2.5Nb tube by the authors were higher than that of a CANDU Zr–2.5Nb tube, as shown in Fig. 1, which turns out to be closer to TSSD rather than TSSP1. Therefore, the authors should define the cooling solvus at the crack tip as TSSD rather than TSSP1, which Kim has already demonstrated [7]. This statement is rather rational because precipitation of the hydrides should antecede at the crack tip before a cooling to T_{c}. Besides, the authors' assumption that the cooling solvus at the crack tip is 0.9 TSSP1 for the RBMK tube and 1.0 TSSP1 for the CANDU tube seems to be hardly rational. In fact, this hypothesis would cause $E(L) - E(l)$, or ΔC between the bulk and crack tip, to increase, leading the RBMK tube to have an increased V_{p} when compared to the case when 1.0 TSSP1 is assumed at the crack tip of the RBMK tube like that at the crack tip of the CANDU tube. This will contribute to a reduction of a difference in V_{p} between the CANDU and RBMK tubes.

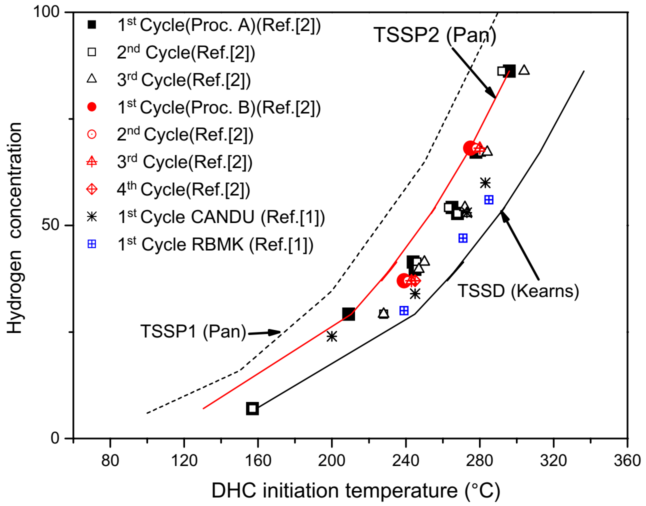

Fig. 1. Comparison of the measured T_{c} data of the CANDU and RBMK Zr–2.5Nb tubes by the authors [1] with those of a CANDU Zr–2.5Nb tube by Shi [2].

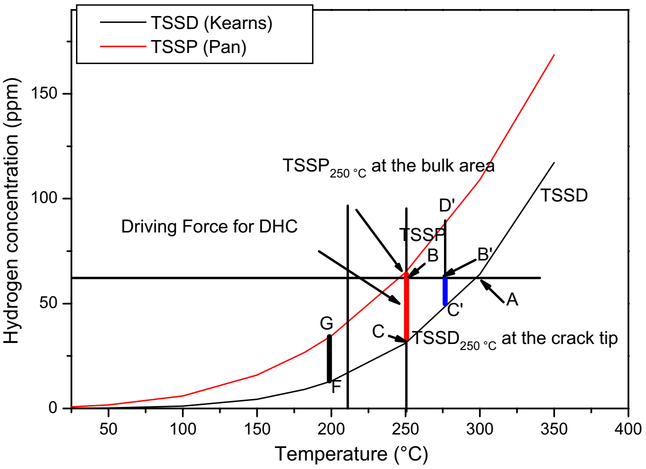

Fig. 2. (a) A difference in the hydrogen concentration or ΔC between the crack tip and the bulk with the test temperatures in Zr–2.5Nb tubes when subjected to DHC tests with the test temperatures approached by a cooling: the ΔC corresponds to GF at 200 °C or BC at 250 °C, but is reduced to B′C′ with the test temperature increasing to 275 °C according to Kim's DHC model [4–6] demonstrating that the ΔC is created by stress induced precipitation of crack tip hydrides.

Since the authors used a single specimen with a fixed hydrogen concentration to measure the crack propagation rate, V_p at different test temperatures, ΔC, driving force for DHC, should decrease with increasing temperature in accordance with Kim's DHC model. For example, when the Zr–2.5Nb specimen with C_o or the initial hydrogen concentration is cooled down to test temperatures that are lower than or equal to 250 °C, the ΔC corresponds to C_o-TSSD (distance BC) or TSSP–TSSD (distance FG) at these test temperatures when TSSP is lower than C_o, as shown in Fig. 2. However, when the test temperature increases to 275 °C, for example, the ΔC decreases to the distance B′C′ when compared to the ΔC_{max}, the maximum driving force corresponding to the distance C′D′ at a constant hydrogen concentration. By plotting the ratio of ΔC over ΔC_{max}, and V_p with the test temperatures, the ΔC dependencies of V_p for both tubes were determined as shown in Figs. 3 and 4. It was found that for both tubes, a decrease of V_p with increasing temperature is due to a decrease in the driving force or a decrease of $\Delta C/\Delta C_{max}$. The minimum driving force or ΔC_{min} for a CANDU Zr–2.5Nb tube over which its V_p had a positive temperature dependency was 0.6 to 0.7 ΔC_{max} over the investigated temperature range (Fig. 3). For the RBMK Zr–2.5Nb tube, the ΔC_{min} varied from 0.5 ΔC_{max} to 0.8 ΔC_{max} with the test temperatures. When the ΔC became higher than the ΔC_{min}, then V_p showed a positive temperature dependency for both tubes, as shown in Figs. 3 and 4. It should be noted that the uncertainty of ΔC_{min} depends strongly on the accuracy of the measured hydrogen concentration of the specimens.

The authors showed that the activation energies of V_p for the CANDU and RBMK tubes were the same ranging from 66 to 68 kJ/mol, which is in contrast with the activation energy of V_p determined using more than 200 measured data of V_p for the same tube. Round robin tests on DHC velocity of the same CANDU and RBMK Zr–2.5Nb tubes have shown that the activation energy of V_p is 47.9 kJ/mol for the CANDU Zr–2.5Nb tube and 55.5 kJ/mol for the RBMK Zr–2.5Nb tube when all the V_p data corresponding to around 260 are accounted for [10]. Thus, it is concluded that the single specimen method used by the authors is so unreliable as to produce erroneous V_p data and its activation energy.

Eq. (1) can be rewritten to determine a temperature dependency of V_p as in the following:

$$V_p = 2\pi k D \Delta C, \tag{3}$$

where D is hydrogen diffusivity, ΔC a difference in the hydrogen concentration between the bulk and the crack tip and k is $1/\Omega_{Zr}\phi(L,l)t_{hyd}N_H x$, which is a constant, independent of temperature. Thus, the activation energy, Q_V of V_p should be determined mainly by the activation energy, Q_D of the hydrogen diffusivity and the activation energy, $Q_{\Delta C}$ of ΔC, if any. Since the authors simply assumed a lower Q_D for the CANDU tube than that for the RBMK tube as shown in Table 7 [1], $Q_{\Delta C}$ of ΔC for the CANDU tube should be larger than that for the RBMK tube to make Q_V identical for both tubes. However, since ΔC is determined from cooling solubility (or TSSP2) and heating solubility (TSSD) of zirconium alloys, it is more rational to assume that ΔC should be the same for both Zr–2.5Nb tubes

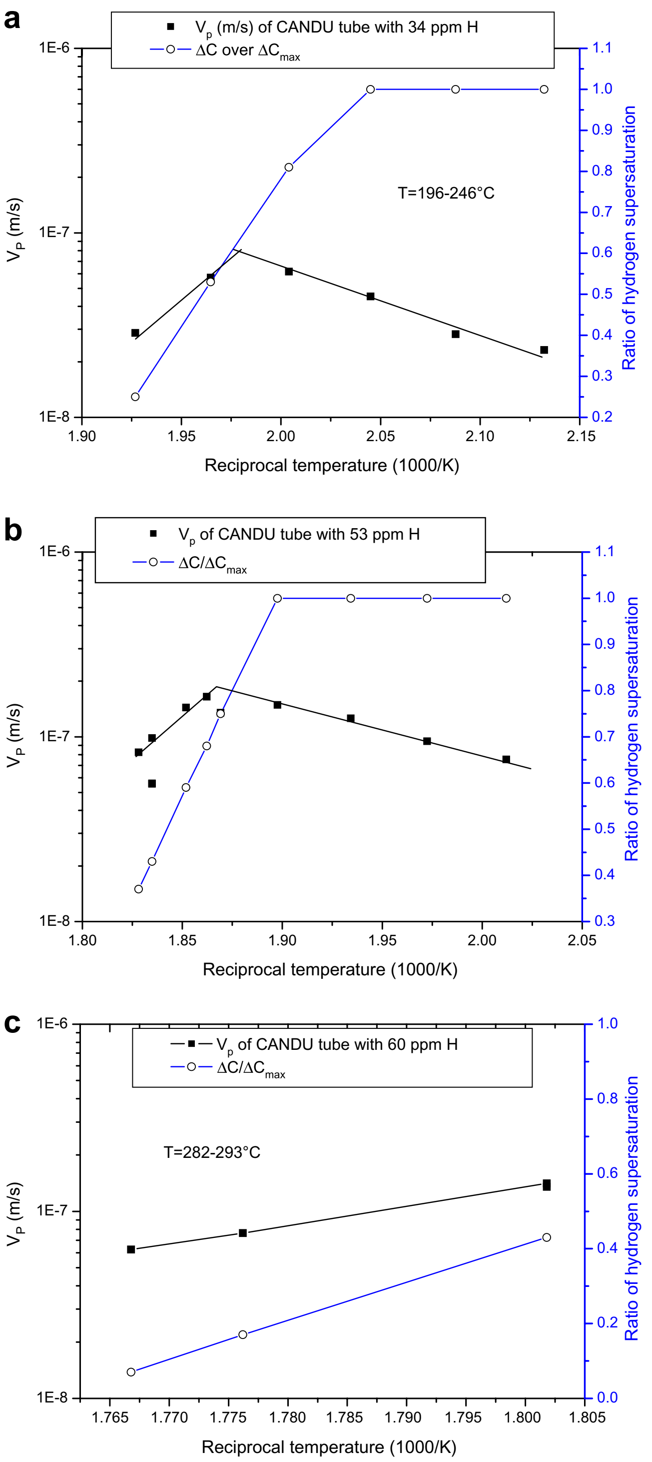

Fig. 3. Temperature dependency of the crack propagation rate, V_p and the ratio of a hydrogen supersaturation ($=\Delta C/\Delta C_{max}$) for a CANDU Zr–2.5Nb tube with (a) 34 ppm H, (b) 53 ppm H and (c) 60 ppm H. Here ΔC_{max} and ΔC correspond to TSSP2–TSSD and C_o-TSSD, respectively, at a given temperature.

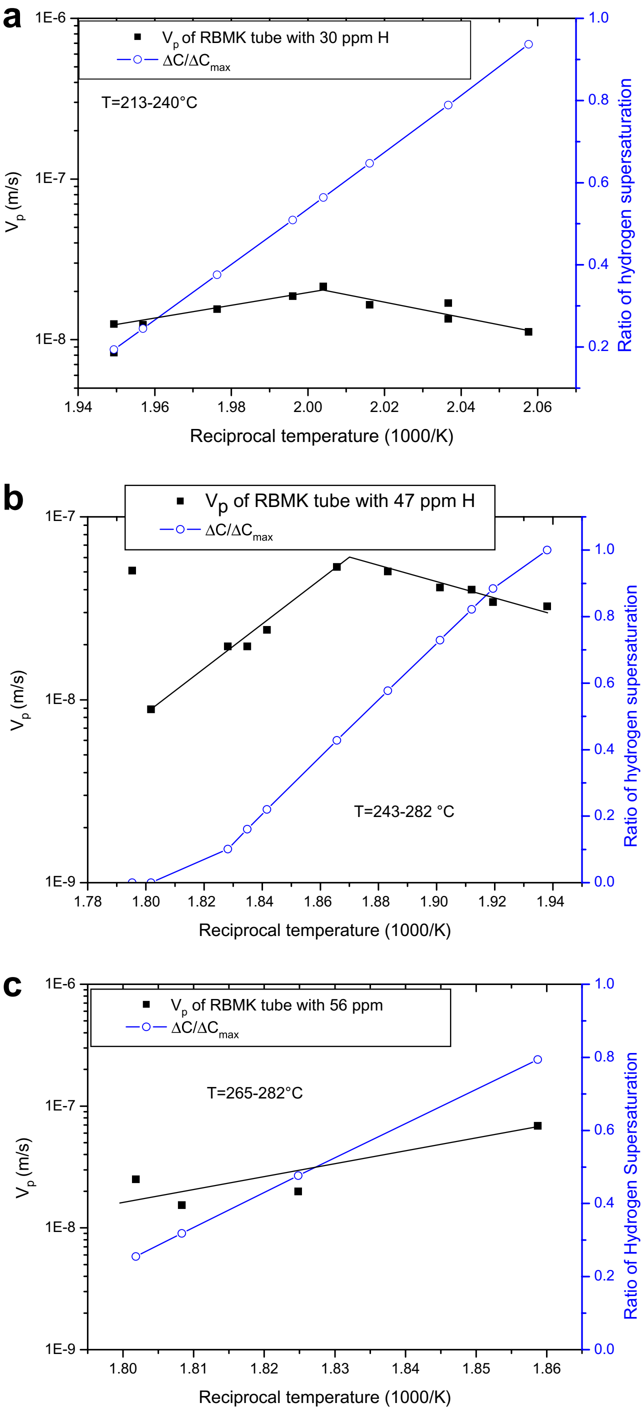

Fig. 4. Temperature dependency of the crack propagation rate, V_p and the ratio of a hydrogen supersaturation ($=\Delta C/\Delta C_{max}$) for a RBMK Zr–2.5Nb tube with (a) 30 ppm H, (b) 47 ppm H and (c) 56 ppm H, where ΔC_{max} and ΔC correspond to TSSP2–TSSD and C_o-TSSD, respectively, at a given temperature.

independent of the metallurgical variables. In other words, $Q_{\Delta C}$ of ΔC, if any, should be the same for CANDU and RBMK tubes. Hence, it is more rational to conclude that Q_V should be governed only by Q_D if Eq. (1) is valid. This conclusion may demonstrate the plausibility of one of the authors' conclusions that a lower V_p of the RBMK tube by 65–80% when compared to that of the CANDU tube is mainly due to a lower D_H in the RBMK tube. However, the problem is that this conclusion cannot account for the authors' results that both tubes have the same Q_V despite their Q_D being different. This contradiction is due to some uncertainty in the V_p data that the authors determined using the single specimen method. Concrete evidence for this statement is provided by comparing the thermal dependencies of V_p data for the same CANDU and RBMK tubes that were determined by the authors and through the IAEA round robin tests, respectively.

3. Conclusions

Reanalysis of Eq. (1) established using Puls's DHC model shows that the activation energy of V_p should be different between the CANDU and RBMK tubes due to their different hydrogen diffusivities, which is contradiction with the same activation energies for V_p of both tubes by the authors. This difference seems to come from some uncertainties in the measured V_p that the authors determined with the single specimen method. Evidence for this comment is provided by comparing the thermal dependencies of V_p for the same CANDU and RBMK tubes that were determined by the authors and through the IAEA round robin tests, respectively. Using Kim's DHC model, it is demonstrated that a negative temperature dependency of V_p at above T(max V_p) for both Zr–2.5Nb tubes is due to a decreased hydrogen supersaturation below ΔC_{min} over which V_p becomes independent of hydrogen concentrations.

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References

[1] P. Cirimello, G. Domizzi, R. Haddad, J. Nucl. Mater. 350 (2006) 135.
[2] S.Q. Shi, G.K. Shek, M.P. Puls, J. Nucl. Mater. 218 (1995) 189.
[3] M.P. Puls, Metall. Trans. A 21 (1990) 2905.
[4] Y.S. Kim, S.S. Kim, S.B. Ahn, et al., Abstract booklet for 14th Symposium on Zirconium in the Nuclear Industry ASTM Stockholm, 2004, p. 81.
[5] Y.S. Kim, Metals and Materials Int. 11 (2005) 29.
[6] Y.S. Kim, S.B. Ahn, Y.M. Cheong, J. Alloys and Comp. 429 (2007) 221.
[7] Y.S. Kim, Mater. Sci. Eng. A 468–470 (2007) 281.
[8] J.J. Kearns, J. Nucl. Mater. 22 (1967) 292.
[9] Z.I. Pan, I.G. Ritchie, M.P. Puls, J. Nucl. Mater. 228 (1996) 227.
[10] Delayed hydride cracking in zirconium alloys in pressure tube nuclear reactors, IAEA TECDOC 1410, Final report of a coordinated research project, 1998–2002, October, 2004.