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Reply to Young S. Kim: 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

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We appreciate the interest of Dr. Y.S. Kim in analyzing our paper [1] but we found that several points have not been well understood or erroneously interpreted. The objective of this response is to clarify all these points within the possibilities of a letter to the editors.

In first place, Dr. Kim considered that Shi's models about critical temperature T_c [2] is different from Puls's models [3,4] for predicting crack propagation velocity V_p. In our opinion, both theories are based on the same concept: the hydrogen diffusion to the crack tip, induced by the stress gradient, and subsequent hydride precipitation at the tip when hydrogen concentration is high enough to equal the terminal solid solubility for precipitation TSSP.

The only difference between T_c and V_p calculus resides in the fact that, when approaching to the test temperature from above the temperature of dissolution, in order to determine T_c, all the hydrogen is in solution, even in the crack tip. So, the hydrogen concentration at the crack tip is increased by the interaction between tensile stress and hydrogen in solution $(p(L,l)\overline{V}_H)$ until the solvus for precipitation is reached and the hydride precipitation occurs.

Alternatively, when the crack is propagating at a temperature lower than T_c, hydride precipitates are present in the bulk and crack tip; then, hydride particles interact with the tensile stress and the solubility decreases due to the stress potential: $\overline{W}_t^a(L,l) = -\overline{V}_{\text{hid}}\sum\sigma_{i,j}e_{i,j}$. As the stresses are much higher near the crack tip than in the bulk, the term $(E(L)-E(\text{l}))$ in Eq. 8 of [3] becomes positive and acts as a driven force for hydrogen diffusion and crack propagation.

In fact, Puls's model was developed to evaluate the crack propagation when hydride particles are present in the material bulk; under this condition V_p vs. temperature behavior is reproduced by an Arrhenius law. This happens for temperatures lower than that corresponding to the maximum V_p for each hydrogen concentration. In this temperature range, the experimental data measured in CANDU and RBMK Pressure Tubes [1] were well adjusted by Puls's equation [3,4], using the TSSP1 and TSSP2 solvus curves measured by Pan et al. [5], at the crack tip and in the bulk, respectively (Fig. 10 of [1]). In addition, the data obtained at temperatures higher than $T(V_p\text{max})$ were qualitatively reproduced for specimens with two different hydrogen concentrations by replacing TSSP2 by the hydrogen concentration of each specimen (Fig. 11 of [1]). It is important to consider that this last assumption was also used by Kim in his "Comment..." to reproduced the V_p behavior at higher temperatures, but cannot explain the Arrhenius behavior at lower temperatures (see Figs. 3 and 4 of his Comment).

It seems that Dr. Kim confuses the hydride thickness (1–1.5 μm) with the radius "*l*" of the hydrogen sink; in the calculation of Eq. 5 of [1], this was actually chosen as the striation length (20 μm) not 1 or 1.5 μm as he suggests in his comment. The hydride thickness (t_{hyd}) is used in eq. 5, but out of the term (E(L)− E(l)) and it is not related to the plastic zone size at all.

As it is well known, in pressure tubes hydride plates precipitate on the circumferential–axial (C–A) plane, while, in CCT specimens the hydride particles precipitating at the crack tip are parallel to the radial–axial (R–A) plane. In addition, when hydride dissolution is produced at relatively

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low temperatures (lower than 400 °C) the hydride nuclei remains in the matrix (memory effect) and the precipitation during cooling occurs at a hydrogen concentration (TSSP2) lower than that required when the nuclei must be formed (TSSP1) [5]. Then, the selection of TSSP1 at the crack tip and TSSP2 at the bulk is quite reasonable, because it establishes the different solvus of hydride particles that nucleate in the crack tip, with respect to the precipitation in the rest of the material. In the first case, assuming that the hydrides precipitated in the previous propagation step are completely cracked, the new ones will precipitate perpendicular to the applied stresses, on the R–A plane where no previous particle exists. Precipitation in the bulk, instead, will proceed on the plane C–A where the nuclei were not dissolved during the thermal cycle.

The solvus curves TSSP1 and TSSP2 were measured for CANDU tubes but these curves were not available for RBMK tubes. Taking into account that the precipitation is associated to the matrix-particle accommodation energy and that this is proportional to the yield stress, the TSSP1 and TSSP2 curves for RBMK were estimated 10% lower than CANDU TSSP1 and TSSP2, because of the lower yield stress of RBMK. This assumption is in good accord with the hydrogen concentration measured by Makaravicius et al. [6] in CANDU and RBMK PTs. Not only it explains the higher values of T_c for RBMK (Fig. 6 of [1]) but also produces a reduction of 10% on V_p values as shown in Fig. 10(b) of [1]. The difference between T_c of both CANDU PTs, (the one used in our work [1] and that used by Shi et al. [2]) is easily explained when their different yield stress (σ) values are introduced in Shi's T_c equation, as is shown in the label of Fig. 6 in [1].

The facts that the T_c values measured in [1] are closer to the TSSD and that T_c is higher than precipitation temperature (TSSP1) are used by Dr. Kim as an argument against the option of using TSSP1 as the solvus curve for precipitation at the crack tip, instead of TSSD as he postulates in his theory. It seems that there is a confusion in this topic because the critical concentration for a given temperature (curve H concentration vs T_c) is the hydrogen concentration in the "bulk" (not at the crack tip) that the material must have in order to attain the precipitation (TSSP1) at the crack tip, assisted by the tensile stress term: $p(L,l)\overline{V}_H$, as can be seen in the Eq. 24 of [2].

Another objection made by Dr. Kim to the V_p values measured in [1] is the use of a single specimen to measure V_p at different temperatures. However, the values reported in Figs. 8 and 9 of [1] correspond to several specimens with different hydrogen concentrations and two different procedures, as described in Section 2.3 of [1]. In procedure (b), after measuring V_p at a temperature, the specimen was reheated to a temperature higher than TSSD and then cooled to a new test temperature, according to the recommendation of IAEA Round Robin [7] (IAEA RR) of approaching to test temperature from above with a ΔT higher than 50 °C.

Finally, the values obtained in [1] have been considered as erroneous by Dr. Kim, on the basis that the activation energy measured in the IAEA RR tests [7] are lower than that measured in [1]. In Fig. 1 the data reported in [7] are represented together with our own values and the theoretical curve. As can be seen, the Argentinean values fall in the range of dispersion of other laboratories, for 283 °C all V_p values are lower than those predicted (Argentinean values included). One possible reason for this result is that the hydrogen concentrations of the specimens used to measure V_p at the higher temperatures were too low and hydride precipitation did not occur at test temperature, producing slower crack propagation rates than the V_p max for each hydrogen concentration. Note that the same behavior is reported for RBMK values (Fig. 2). In the IAEA RR [7] tests the measured hydrogen concentration values were highly variable and did not correlate well with the expected values based on Kearns SSTD curve (See Fig. 4.7 of [7]), hydrogen concentration as low as 40 ppm were measured when the expected values were 80 ppm. The lower V_p

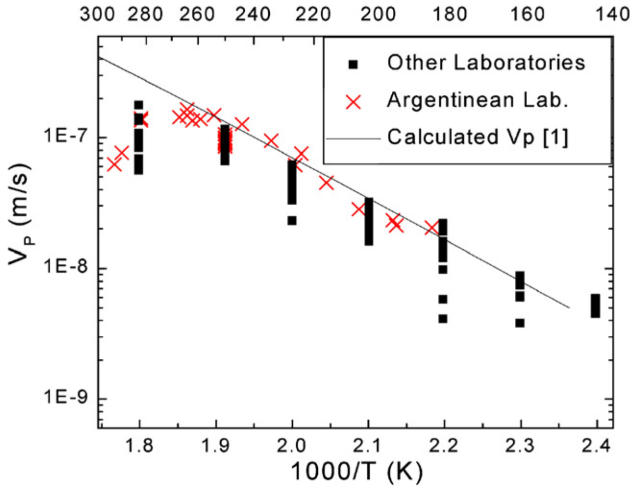

Fig. 1. V_p values measured in CANDU Pressure tube by ten countries participating in IAEA Round Robin test [7], including Argentinean laboratory and calculated curve [1].

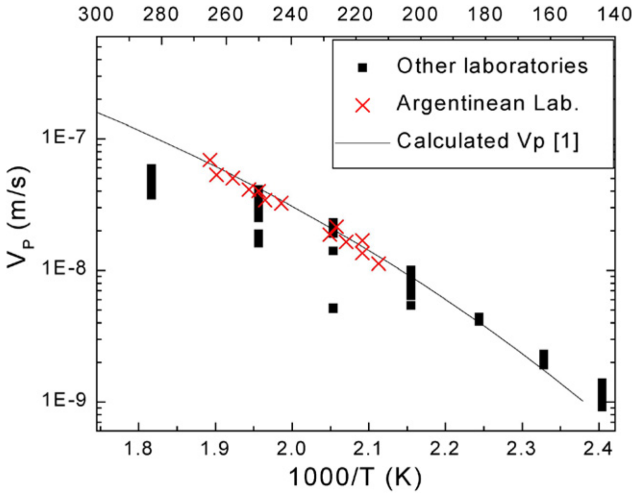

Fig. 2. V_p values measured in RBMK Pressure Tube by ten countries participating in IAEA Round Robin test [7], including Argentinean laboratory and calculated curve [1].

Table 1
Activation energies of solubility (C_H), diffusion (D_H) and interaction energy per mole of hydrogen due to hydride formation under external stresses ($\overline{W}_t^a(L,l)$) used in V_p Eq. (5) of [1]

r	T (°C)	$C_H = A\exp(Q/RT)$		$\overline{W}_t^a(L,l)$		$D_H = D_o\exp(Q_D/RT)$		$Q+\overline{W}_t^a(L,l)+Q_D$	
		Q of TSSP1	Q of TSSP2	CANDU	RBMK	Q_D CANDU	Q_D RBMK	CANDU	RBMK
L	150		−27.99	−1.4	−1.4	−34.72	−42.44	−64.11	−71.83
L	300		−27.99	−1.3	−1.3	−34.72	−42.44	−64.01	−71.73
l	150	−25.84		−5.0	−4.3	−34.72	−42.44	−65.56	−72.58
l	300	−25.84		−3.9	−3.6	−34.72	−42.44	−64.46	−71.88
Average activation energy								−64.5	−71.9

values measured at the higher temperatures are responsible of the lower slope of Arrhenius fitting measured in the IAEA RR [7].

As mentioned above, the V_p values vs T can be correlated by an Arrhenius equation for temperatures lower than $T(V_p\text{max})$ with an activation energy of $Q = -65.8$ KJ/mol K for CANDU material and $Q = -67.2$ KJ/mol K for RBMK (Figs. 8 and 9 of [1]). Both these two set of values can be adjusted by Puls's model [3] too (Fig. 10 of [1]). The different activation parameters used in Puls's V_p formula (Eqs. (8), (9), and (10) of Ref. [3]), with the assumptions made in our paper [1], are listed in Table 1 in the temperature range of 150 to 300 °C. This clearly shows how the stress term $\overline{W}_t^a(L,l)$ compensates the different values of the solubility TSSP far (L) and near (l) the crack tip, allowing V_p to be adjusted by an Arrhenius equation with an average activation energy of 65 KJ/mol K for CANDU and 72 KJ/mol K for RBMK, which is in good agreement with the values reported in [1].

In conclusion, the V_p equation calculated by Puls [3], used with the assumptions introduced in [1], is capable of predicting with good agreement the experimental values measured in two pressure tubes (CANDU and RBMK) by our laboratory and those measured in the frame of an IAEA research project, excepting those specimens with insufficient hydrogen to have hydride particles precipitated at test temperature.

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