

Delayed Hydride Cracking Mechanism in Zirconium Alloys and Technical Requirements for In-Service Evaluation of Zr-2.5Nb Tubes with Flaws

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1. DHC Evaluation Procedures in CSA N285.8 [1]

In association with periodic inspection of CANDU nuclear power plant components, Canadian Standards Association issued CSA N285.8 in 2005 as technical requirements for in-service evaluation of zirconium alloy pressure tubes in CANDU reactors. This first version, CSA N285.8 involves procedures for, firstly, the evaluation of pressure tube flaws, secondly, the evaluation of pressure tube to calandria tube contact and, thirdly, the assessment of a reactor core, and material properties and derived quantities.

The evaluation of pressure tube flaws includes delayed hydride cracking evaluation the procedures of which are stipulated based on the existing delayed hydride cracking models. For example, the evaluation of flaw-tip hydride precipitation during reactor cool-down involves a procedure to calculate the equilibrium hydrogen equivalent concentration in solution at the flaw tip, H_{tip} , as follows:

$$H_{tip} = H_f \exp[-(V_H \Delta \sigma) / RT], \quad (1)$$

where H_f is the total bulk hydrogen equivalent concentration, V_H partial molar volume of hydrogen in zirconium, $\Delta \sigma$ a difference in hydrostatic stress between the bulk and the crack tip. When $H_{tip} \geq TSSP$ at temperature, then flaw-tip hydride is predicted to precipitate. Eq. (1) suggests that hydrogen concentration at the crack tip would increase due to an work energy given by the difference in the hydrostatic stress.

However, Eq. (1) is established [2] based on Li et al.'s paper [3] where the hydrostatic stress arising from precipitating hydrides with a larger volume suppresses precipitation of the hydrides, causing supersaturation of hydrogen in the zirconium matrix. In other words, Eq.(1) accounts for the increased hydrogen solubility upon precipitation of hydrides due to the hydrostatic stress, which has nothing to do with the movement of hydrogen to the stressed region such as the crack tip. Actually, Eq. (1) provides a theoretical rationale for a higher hydrogen solubility on a cooling compared to that on a heating due to a lattice misfit. $V_H \Delta \sigma_h$ in Eq. (1) is the work energy due a lattice misfit which Birnbaum [4] and Puls [5,6] have defined as \bar{W}_i^{inc} , the total molal strain energy required to make room for the expansion of the hydride. Eq(1) can be expressed by using \bar{W}_i^{inc} as such:

$$C_H^{con} = C_H^o \exp(\bar{W}_i^{inc} / RT) \quad (2)$$

where C_H^{con} is the constrained solvus that is increased by a factor depending on \bar{W}_i^{inc} , C_H^o is the solvus in a unconstrained state. It should be noted that the magnitude of \bar{W}_i^{inc} may depend on the number of hydrogen atoms, x in a mole of the hydride with composition ZrH_x . Thus, applied tensile stresses will compensate for \bar{W}_i^{inc} , reducing the constrained solvus to finally the unconstrained solvus. Similar argument was suggested by Puls [5,6]. He suggested a shift in the cooling solvus to a higher temperature due to applied stresses in zirconium and its alloys according to the following equation:

$$C_H^{Con,\sigma} \equiv C_H^{Con} \exp(W_i^a / xRT) = C_H^S \exp\{[\bar{W}_i^{inc} + W_i^a(l)] / xRT\} \quad (3)$$

where $C_H^{Con} = C_H^S \{\bar{W}_i^{inc} / xRT\}$, $C_H^{Con,\sigma}$ and C_H^{Con} are the cooling terminal solid solubility (TSSP) of hydrogen with and without applied stress, respectively, C_H^S is the heating terminal solid solubility (TSSD), \bar{W}_i^a the interaction energy of the hydride by applied stresses, and T is the temperature (K). Especially, when $\bar{W}_i^{inc} \approx -\bar{W}_i^a$, then $C_H^{Con,\sigma} \equiv C_H^S$ from Eq. (3) [6]. In other words, Puls has shown that the effective terminal solid solubility (TSS) for the crack tip hydride is reduced to the stress-free TSS, C_H^S [5] due to the applied stress. In short, all the theoretical analyses and experimental facts have demonstrated that a reduction of the chemical potential or chemical free energy by applied stresses is the driving force for enhanced precipitation of the hydrides at the crack tip. Therefore, the effect of tensile stresses is to enhance precipitation of hydrides in metal matrix, reducing the supersaturated hydrogen concentration in the stressed region to the unconstrained solubility or TSSD, not to move hydrogen to the crack tip as described in Eq. (1).

2. Kim's DHC Model

Contrary to the previous DHC models, for the first time, Kim et al. [7,8] suggested a new DHC model that an applied stress promotes precipitation of the hydrides in the zirconium matrix rather than hydrogen migration to the crack tip from the bulk region. Thus, the first process of DHC should be precipitation of the hydrides at the crack tip only, followed by the migration of hydrogen from the bulk region to the crack tip as opposed to the contention of the previous DHC models. This suggestion appears to agree with Flanagan's theoretical analysis demonstrating that the hydride

phase can precipitate in the stressed volume such as the crack tip region [9]. A sufficient condition for hydride precipitation is a supersaturation of hydrogen either by undercooling or ΔT from the TSSD temperature or by increasing the charged hydrogen concentration by an increase of the hydrogen gas pressure in an isothermal condition when no transformation of hydrides is considered. Since the hydrogen gas pressure and the dissolved hydrogen concentration are constant during DHC tests for zirconium alloys, the only way to establish a supersaturation of hydrogen is some undercooling from the TSSD temperature. In other words, precipitation of the hydrides won't occur simply with the C_{HL} increasing to the C_p by a stress difference since at an equilibrium the chemical potential of hydrogen at the crack tip is equal to that in the bulk region [9]. A rationale for a preferential precipitation of the hydrides at the crack tip is provided by the observation [10] that dislocations or slip bands formed in the plastic zone have facilitated precipitation of hydrides, likely by accommodating strains induced by precipitation of the hydrides with a larger volume. Preferential precipitation of the hydrides at the crack tip, as assumed by Kim's DHC model [7,8], lets the supersaturated hydrogen concentration at the crack tip decrease to the hydrogen concentration corresponding to the TSSD at the test temperature or point C [8], causing a hydrogen concentration difference or ΔC between the crack tip and the bulk region, corresponding to the distance BC as shown in Fig. 1. This is the driving force for DHC according to Kim's DHC model.

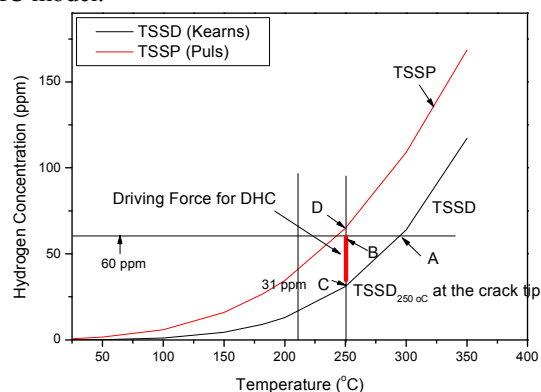


Figure 1. (a) The solvus lines of hydrogen during a thermal cycle to which the Zr-2.5Nb with 60 ppm H is subjected in DHC tests. The driving force for DHC is a difference in hydrogen concentration or ΔC accompanied by nucleation of the hydrides at the crack tip under a tensile stress, which corresponds to 29 ppm H at 250 °C, equal to the distance BC.

4. Conclusion

It is found that the evaluation procedure for pressure tube flaws as stipulated in CSA N285.8 is established based on the existing DHC models. According to the

so-called Kim's DHC model, however, tensile stresses cannot cause hydrogen to move towards the crack tip but promotes precipitation of the hydrides at the crack tip, leading the hydrogen concentration at the crack tip to decrease to the heating solvus of hydrogen or the TSSD. Hence, the evaluation procedures for pressure tube flaws of CSA N285.8 should be revised in accordance with Kim's DHC model.

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