

Review of DHC Initiation and Arrest Temperatures for Zr-2.5Nb Tubes

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1. Introduction

As Shi and Puls proposed a DHC model [1] where the driving force for a DHC is a tensile stress gradient, leading the hydrogen concentration at the crack tip to increase to the terminal solid solubility of precipitation (TSSP) of hydrogen accompanied by a decrease in the hydrogen concentration dissolved in the bulk region. Based on their DHC model, Shi et al. [2] conducted a series of tests and a theoretical analysis with an aim to define the hydrogen concentration limit as a function of the temperature where the delayed hydride cracking commences and stops in the Zr-2.5Nb pressure tube. They reported that the DHC initiation and arrest temperatures, T_c and T_h , respectively are close to but below, the temperatures defined by the terminal solid solubility for dissolution (TSSD) [3] for the hydrogen concentrations of the specimens which is in contrast with the Coleman's result. Furthermore, they suggested that the reason for the closeness of the T_c to the TSSD temperatures resides in the shift of the solvus due to the hysteresis between the hydride precipitation and dissolution and the opposite effect of the stress by increasing the hydrogen concentration at regions of a high tensile stress.

The problem with their DHC model is that the crack tip cannot reach the TSSP with the test temperature approached by heating under any stress gradient and the assumption that the tensile stress acts as a hydrostatic stress is unrealistic. Instead, Kim propose a new DHC model where the driving force for the DHC is a difference in the hydrogen concentration by nucleating the hydrides, preferentially only at the crack tip under an applied tensile stress [4,5] which is attributed to a hysteresis of the terminal solid solubility of hydrogen on a heat-up and a cool-down. Thus, the objective of this paper is to reanalyze the hydrogen concentration limit and the critical temperatures for the DHC in zirconium alloys reported by Shi et al. [2] using the Kim's DHC model [4,5].

2. Re-Analysis

We plotted the hydrogen concentration as a function of the measured T_c and T_h along with the TSSD [3] and TSSP lines [6] using the data shown in Table 2 in [2]. The results shown in Fig. 1 demonstrate that the DHC initiation temperatures, T_c generally follow the TSSP2 line except for at as low a hydrogen concentration as 7 ppm H, which is in contrast with the argument of Shi et al. [2]. Here, the TSSP1 and TSSP2 data are taken from [6], each of which is defined as the terminal solid solubility of hydrogen on a cool-down from 450 °C and the peak temperature in excess of 50 °C over the TSSD, respectively. Especially, at the 29.2 ppm hydrogen, the measured T_c after the 1st cycle of procedure A exactly agrees with the TSSP2 temperature reported by Pan et al. which was measured with the peak temperature in excess of 50-60 °C over the TSSD temperature. However, this fact does not coincide with the argument by Shi et al [2] that the TSSP1 was obtained by cooling from 450 °C and at least 50 °C above the TSSD. A confusion of the TSSP1 and the TSSP2 has led them to argue that the T_c and the T_h are close to but below, the temperatures defined by the terminal solid solubility for

dissolution (TSSD). Another thing to note is that the T_c increases with an increasing thermal cycle towards the TSSD temperature, which holds true at all the hydrogen concentrations.

In contrast, the theoretical analysis for the DHC initiation temperature, T_c was carried out based on the assumption that a tensile stress gradient lets the hydrogen dissolved in the bulk move up to the crack tip and causes hydrides to precipitate. As shown in Fig. 1, however, it turns out that the calculated T_c generally deviates from the TSSP2 line. The discord between the measured and calculated T_c is likely to be attributed to the invalid assumption that the driving force for the DHC is a tensile stress gradient.

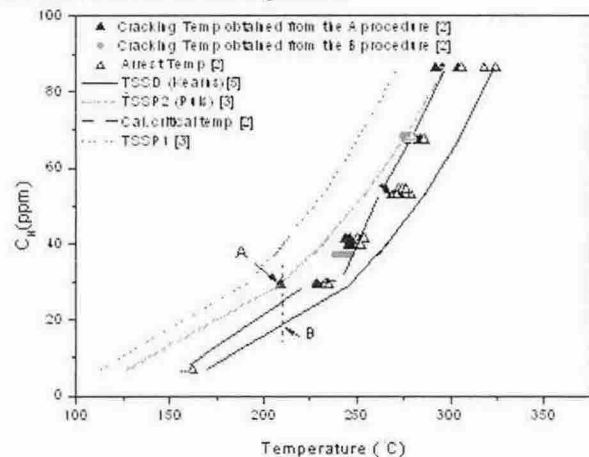


Fig. 1. Hydrogen concentration versus the DHC initiation and arrest temperatures in a Zr-2.5Nb tube [2] along with the TSSD [3] and TSSP [6] temperatures.

3. Discussion

The experimental fact that the T_c agrees with the TSSP2 temperature at a temperature in excess of 180 °C as shown in Fig. 1 demonstrates that the δ -hydrides start precipitation only after the TSSP temperature is reached [7]. Further, the higher T_c with the increased number of the thermal cycles indicates that the plastic deformation generated in the former cycle facilitates the nucleation of the hydrides in the next cycle, leading the TSSP temperatures to move towards the TSSD as shown in Fig. 1. Therefore, we conclude that the nucleation of the hydrides is driven by the combined effect of a degree of supercooling from the TSSD or ΔT and the plastic deformation produced by the applied tensile stress and thermal cycle, not by a tensile stress gradient as suggested by [1,2]. It is because the hydrides can nucleate only if the following condition is satisfied: $\Delta\epsilon_h + \omega_p + \Delta\epsilon_{\text{hydride}} = 0$, where $\Delta\epsilon_h$ is the decreased strain energy by taking the dissolved hydrogen out of the matrix with the supersaturated hydrogen concentration by supercooling, ω_p is the applied plastic work and $\Delta\epsilon_{\text{hydride}}$ is an increase in the strain energy by the nucleating hydrides. This rationale can explain why procedure B with the tensile stress applied at the lower temperature or the lower DHC initiation temperature requires

a slightly larger amount of supercooling when compared to procedure A with the tensile stress applied on a cool-down from 20 °C above the TSSD line as shown in Fig. 1.

When the hydrogen concentration was as low as 7 ppm, surprisingly, the DHC initiation temperature was strongly relevant to the TSSD, not to the TSSP which is also in contrast with the assumption by Shi and Puls [1,2] that the hydrogen concentration at the crack tip reaches the TSSP under a tensile stress gradient. Since γ -hydrides with a lower volume (around 14%) precipitate at a lower hydrogen concentration and a lower temperature than 180 °C [8], then a lesser amount of supercooling will be required for precipitating them. Thus, as soon as the hydrides nucleate at the crack tip, there develops a difference in the hydrogen concentration between the crack tip and the bulk region. This corresponds to the amount of the supersaturated hydrogen concentration, ΔC that is required to precipitate the hydrides in the zirconium lattice. In other words, the ΔC is a driving force for the DHC as already suggested by Kim [3,4].

Since the supersaturation of the hydrogen for the DHC initiation is related to TSSP-TSSD, a dependency of the ΔC on the temperature should follow a thermal dependency of the hysteresis of the TSS of hydrogen (Fig. 2). As expected, the supersaturated hydrogen concentration for the DHC initiation agrees well with the hysteresis of the TSS of hydrogen, providing other supportive evidence that the supersaturation of hydrogen, ΔC is a governing factor for the DHC.

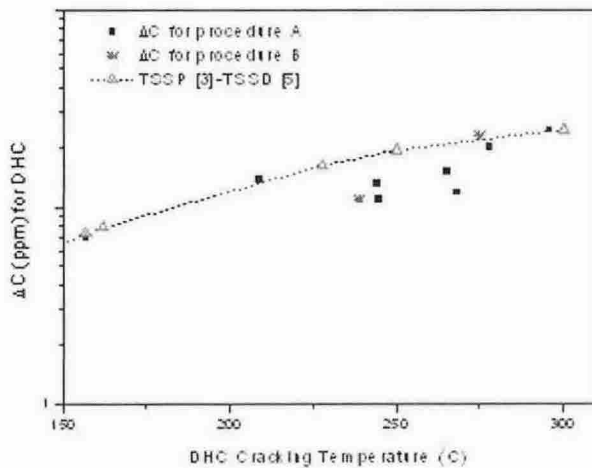


Fig. 2. Coincidence of the temperature dependency of the ΔC for the DHC initiation and that of the TSSP [6]-TSSD [3].

Likewise, we determined the minimum ΔC required for arresting the DHC using the highest T_h ever reached and the initial hydrogen concentration as shown in Table 2 [2]. Fig. 3 shows the minimum ΔC required for arresting the DHC on the heat-up of the specimen after the DHC initiation. It is very interesting to find that the minimum ΔC for the DHC arrest follows a parabolic dependency on the temperature whose general pattern looks very similar to the DHCV-temperature relationship with the test temperature approached by heating as Ambler reported for the first time [9]. This result also confirms that the ΔC is the driving force for the DHC. Since the ΔC corresponds to the TSSP-TSSD as explained above, we plotted the TSSP-TSSD as a function of the temperature as shown in Fig. 5. The ΔC increases with an increasing temperature, levels off at around 300 °C and then decreases at temperatures in excess of 330 °C. The thermal dependency of the ΔC as shown in Fig. 5 turns out to be generally similar to the thermal dependency of the

minimum ΔC for the DHC arrest as shown in Fig. 3. Therefore, we conclude that the ΔC arising from a hysteresis of the terminal solid solubility of hydrogen on a heat-up and a cool-down is the driving force for the DHC.

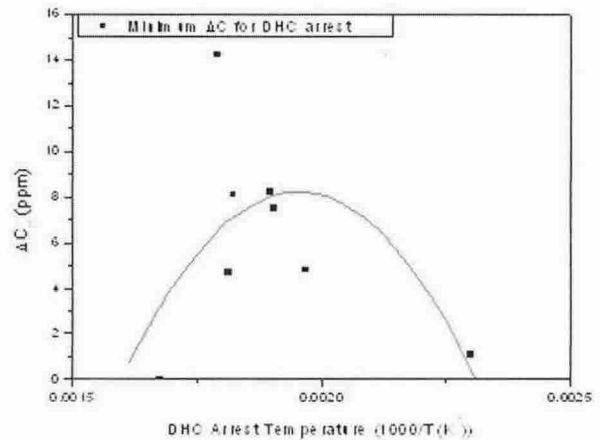


Fig. 3. Minimum supersaturated hydrogen concentration for arresting the DHC in the Zr-2.5Nb tube.

4. Conclusion

The DHC initiation temperatures generally coincide with the TSSP2 temperature [3] and increase towards the TSSD with an increasing number of the thermal cycles, which is in contrast to Shi et al.'s argument [2]. Therefore, using the Kim's DHC model [3,4], we correlated the DHC initiation and arrest temperatures with the critical supersaturated hydrogen concentration or ΔC and conclusively demonstrated that the ΔC for the DHC initiation agrees with the hysteresis of the TSS of hydrogen and a temperature dependency of the minimum ΔC for the DHC arrest coincides with the temperature dependency of the DHC velocity with the test temperature approached by heating.

Acknowledgment

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References

- [1] S.Q. Shi and M.P. Puls MP, J Nucl Mater., Vol. 218, p. 30, 1994..
- [2] S.Q. Shi, G.K. Shek and M.P. Puls, J Nucl Mater., Vol. 218, p. 189, 1995..
- [3] J.J. Kearns, J Nucl Mater., Vol. 22, p. 292, 1976.
- [4] Y.S. Kim et al. to be presented at Proc 14th ASTM Symp Zr in the Nuclear Industry, Stockholm, Sweden, 2004.
- [5] Y.S. Kim et al. TMS 2003 Annual Meeting & Exhibition Program and Guide, San Diego: JOM 55, 2003, p.383.
- [6] Z.L. Pan, I.G. Ritchie and M.P. Puls MP, J Nucl Mater., Vol. 228, p.227, 1996.
- [7] Root JH, Small WM, Khatamian, Woo OT. Acta Mater 2003;51:2041.