Lessons Learned from an Understanding of Delayed Hydride Cracking Mechanism in Zirconium Alloys: Integrity of Spent Fuel Rods Stored at Low Temperatures

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1. Previous DHC models

The previous DHC models [1-3] assumed that hydrides precipitate at the crack tip with the hydrogen concentration increasing to the terminal solid solubility of hydrogen for precipitation or TSSP. An applied tensile stress is assumed to create a hydrostatic stress at the crack tip to pull hydrogen from the bulk region towards the crack tip, thus increasing the hydrogen concentration at the crack tip to the TSSP: the hydrogen concentration at the crack tip increases from the terminal solid solubility for dissolution or TSSD (point C) to the TSSP (point E), corresponding to an increase of the hydrogen concentration from C to E as shown in Fig. 1. The theoretical calculation [4] shows that the increased hydrogen concentration at the crack tip is not enough to reach the TSSP. Then, they [5] argued that an approach to the temperature by a cooling is indispensable to let the bulk region reach the hydrogen concentration over the TSSD, corresponding to point B, for the crack tip to increase from point B to the TSSP or point E under a tensile stress (Fig. 1). However, there are weak points with these arguments: firstly, the hydrides cannot precipitate in the zirconium matrix simply with the crack tip reaching the hydrogen concentration corresponding to the TSSP (point E) as assumed in the models. Secondly, DHC at temperatures below 180 ^{o}C upon an approach by a heating cannot be understood with the DHC models proposed so far because the ratio of the TSSP over the TSSD becomes larger with a decreasing temperature. Even though it is conceded that the hydrides can precipitate at the crack tip due to a tensile stress that causes the hydrogen concentration at the crack tip to increase to the TSSP, there are still many unresolved issues related to the DHC of zirconium alloys: firstly, the constant DHC velocity independent of an applied stress intensity factor though a tensile difference is assumed to be the driving force for DHC [1-3], a dependency of the DHC velocity (DHCV) on the direction of an approach to the test temperature [6], a lower activation energy for the DHCV than that predicted by the DHC models [3,7] and a correlation of a DHCV and a striation spacing [8].

2. Kim's DHC model

Kim suggested a new DHC model [9,10] where a driving force for DHC is a supersaturated hydrogen concentration resulting either from a cooling from the TSSD or from the stress-induced hydride transformation from γ to δ. In contrast with what the previous DHC
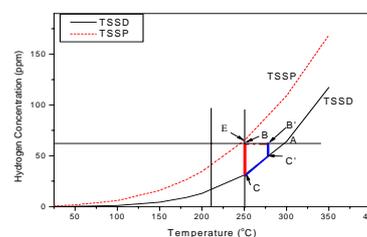
Fig. 1. Schematic diagram for an illustration of the solvus lines that the crack tip and the bulk region take during DHC tests on the Zr-2.5Nb tubes.
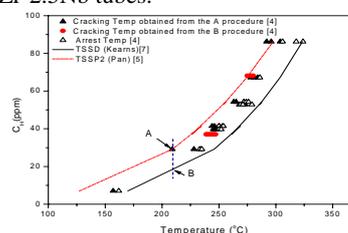
Fig. 2. DHC initiation and arrest temperatures with hydrogen concentrations in the Zr-2.5Nb tube that was subjected to the unratcheting thermal cycle.

models suggested, this new model suggests that a cooling or ΔT from the TSSD temperature to the TSSP temperature is required to create a supersaturation of hydrogen or ΔC, leading the hydrides to precipitate only at the crack tip and the DHC initiation to occur generally at the TSSP temperature. Experimental evidence for this hypothesis is demonstrated in Fig. 2 [11] where the hydrogen concentration is plotted as function of the measured DHC initiation temperature or T_c and DHC arrest temperatures or T_h using the data reported by Shi et al. [4]. According to Kim's DHC model's hypothesis, the DHC initiation temperatures, T_cs generally coincided with the TSSP line except for that at as low a hydrogen concentration as 7 ppm H. This finding explains why DHC only occurs with an approach by a cooling to the test temperatures above 200 ^{o}C where δ-hydrides are present. However, there is a case when DHC can occur without a cooling: at temperatures below 180 ^{o}C, DHC can be initiated near the TSSD temperature as shown in Fig. 2. In this case, a supersaturated hydrogen concentration results from the stress-induced γ to δ transformation at the temperatures below 180 ^{o}C [12] where the γ-hydride phase is present. Since the hydrogen solubility of the γ-hydrides is reported to be higher than that of δ-hydrides [13,14], different distributions of the γ- and δ-hydrides between the crack tip and the bulk region creates a difference in the dissolved hydrogen concentration between the crack tip and the bulk region: a higher

concentration of the dissolved hydrogen in the bulk region and a lower one at the crack tip. This creates the ΔC between the crack tip and the bulk region, thus growing the hydrides at the crack tip to a critical hydride length over which the crack grows by fracturing of hydrides.

3. Cracking of Fuel Rods at RT

Simpson and Ells [15] reported that a Zr-2.5Nb fuel rod had hydrides precipitated at RT at the root of the end cap weld 4 weeks after welding and then a crack extended to about 90% of the cladding wall thickness 2 years after welding. Then they conducted another verification test where a fast growing crack with time was observed at the root of the end cap weld using a cladding tube hydrided to 100 ppm H. The measured crack growth rate turned out to be more than 10^3 times higher than the calculated one by Dutton and Puls's DHC model [15]. They ascribed the disagreement between the measured and calculated crack growth rate, to a large extent to the low hydrogen solubility and low hydrogen diffusivity assumed in the model calculation.

These results definitively demonstrate that hydrides can precipitate even at RT in the region with a high tensile stress of zirconium alloy cladding. Precipitation of hydrides in the zirconium alloy cladding even at RT is similar to the case of DHC at temperatures below 180 ^{o}C that are approached by a heating. A driving force for cracking of zirconium alloy cladding at RT is a supersaturated hydrogen concentration resulting from the stress-induced γ to δ transformation as demonstrated by Kim's DHC model. Direct evidence for the γ to δ transformation is provided by Root [12] who has shown the nucleation of γ-hydrides at as low a temperature as 50 ^{o}C along with a accompanying decrease of the δ-hydrides. When stored at RT for a long time, the δ-hydrides with a large strain energy of 4912 J/mol tends to transform to γ-hydrides with a smaller strain energy of 2662 J/mol [16]. However, this transformation should accompany a hydrogen diffusion into the zirconium matrix so the rate of the δ to γ transformation must be dependent upon the hydrogen diffusivity in the zirconium cladding tube. After a long-term storage at RT, the volume fraction of the γ-hydrides becomes larger with an accompanying decrease of the volume fraction of the δ-hydride except for at the stressed regions like the end cap weld line where the δ to γ transformation is suppressed by a tensile stress. In other words, the whole region in the zirconium alloy tube has many γ-hydrides while the stressed region consists of primarily δ-hydride, thus creating a hydrogen concentration difference between them. Then, hydrogen moves to the stressed region along a hydrogen concentration gradient, leading to the growth of the hydrides to the critical length over which the hydrides fracture.

Since this δ to γ hydride transformation can also occur in the Zircaloy cladding tubes of spent fuel rods during their long-term storage, spent fuel rods stored at RT for a long term may fail as with cracking of the experimental Zr-2.5Nb cladding tubes at RT. Since it is expected that a hydrogen diffusivity is faster in the irradiated Zirycaloy cladding tubes, cracking of the spent fuel rods will occur earlier than expected. It should be noted that all the spent fuel rods may fail unless neither residual stresses nor surface defects with a high stress concentration are present in the cladding tube. Therefore, it is only a matter of time before spent fuel rods experience cracking during their long-term storage if the stressed regions are present.

2. Summary and Further Works

According to Kim's DHC model, failures of Zr-2.5Nb cladding tubes stored at RT turn out to be due to DHC, which cannot be understood with the previous DHC models. The γ to δ hydride transformation causes precipitation of hydrides at the stressed region even at RT, thus creating a supersaturated hydrogen concentration, a driving force for DHC. Since this δ to γ hydride transformation can also occur in the Zircaloy cladding tubes of spent fuel rods during their long-term storage, spent fuel rods stored at RT for a long term may fail as with cracking of the experimental Zr-2.5Nb cladding tubes at RT. Further work is required to establish DHC failure criteria for spent fuel rods that will be stored at low temperatures for a long-term.

REFERENCES
[1] R. Dutton, K.Nuttall, M.P. Puls, L.A. Simpson, Met. Trans. 8A, 1553 (1977).
[2] M.P. Puls, L.A. Simpson, R. Dutton, Fracture Problems and Solutions in the Energy Industry, Ed. L.A. Simpson, Pergamon Press, Oxford, 13 (1982).
[3] C.E. Coleman, J.F.R. Ambler, Reviews on Coatings and Corrosion 3, 105(1979).
[4] S.Q. Shi, G.K. Shek, M.P. Puls, J. Nucl. Mater. **218**, 189 (1995).
[5] R.L. Eadie, C.E. Coleman, Scripta Metall., 23, 1865 (1989),.
[6] J.F.R. Ambler, Zirconium in the Nuclear Industry: Sixth International Symposium, ASTM STP 824, Eds. D.G. Franklin and R.B. Adamson, ASTM, Philadelphia, 653 (1984).
[7] M.T. Jovanovic, R.L. Eadie, Y. Ma, M. Anderson, S. Sagat, V. Perovic, Materials Characterization 47, 259 (2001).
[8] G.K. Shek, M.T. Jovanovich. H. Seahra, Y. Ma, D. Li, R.L. Eadie, J. Nucl. Mater., 221, 226 (1996).
[9] Y.S. Kim, S.S. Kim, S.B. Ahn, Y.M. Cheong, Abstract booklet for 14th Symposium on Zirconium in the Nuclear Industry, ASTM, Stockholm, Sweden, 81 (2004).
[10] Y.S. Kim, Metals and Materials Int. 11, 29 (2005).
[11] Y.S. Kim, Y.M. Cheong, S.J. Choi, Metals and Materials Int. 11, 39 (2005).
[12] J.H. Root, W.M. Small, D. Khatamian, O.T. Woo, Acta Materialia **51**, 2041 (2003).
[13] C.D. Cann, A. Atrens, J. Nucl. Mater., **88**, 42 (1980).
[14] S. Mishra, M.M. Asundi, Zirconium in Nuclear Applications, ASTM STP 551, American Society for Testing and Materials, 63 (1974).
[15] C.J. Simpson, C.E. Ells, J. Nucl. Mater., 52, 289 (1974).
[16] M.P. Puls, Acta Metall., 32, 1259 (1984).