A Model for Delayed Hydride Cracking of Zirconium Alloys

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1. Introduction

One unique feature of delayed hydride cracking (DHC) of zirconium alloys is a constant crack growth rate independent of applied stress intensity factors at the second stage where the applied stress intensity factor far exceeds the critical stress intensity factor, K_{IH} required to initiate DHC Furthermore, this unique feature occurs not only in the DHC process of zirconium alloys but in the hydrogen embrittlement (HE) or the stress corrosion cracking (SCC) of metals. A driving force for all these cracking processes of metals was suggested to be a stress gradient at the crack tip [1,2]. This hypothesis was based on an assumption [2] that an applied tensile stress acted as a hydrostatic tensile stress at the crack tip. However, the problem with this hypothesis is that it cannot explain the constant crack growth rate independent of the applied stress intensity factor in the cracking processes such as DHC, HE and SCC. The aim of this work is to propose a new DHC model which can contribute to a better understanding of the DHC behavior of zirconium alloys including a constant DHCV independent of the applied stress intensity factors at the 2nd stage.

2. New DHC Model

It should be noted that under a stress gradient, the transfer of hydrogen occurs only under thermal cycling, not under thermal annealing at a fixed temperature without any prior cooling [4]. This experimental fact hints some effect of cooling on the hydrogen transfer, which is in conflict with Kammenzind's argument [4].

Zirconium alloys are well known to have a hysteresis of the TSS of hydrogen on heat-up and cool-down due to a volume difference of around 17% between the δ-zirconium hydrides and the zirconium matrix as shown in Fig. 1 [5]. Though the zirconium lattice is contracted on cooling with a driving force to precipitate dissolved hydrogen into hydrides, the increased lattice strain energy resulting from the precipitating hydrides with a larger volume by around 17%, thus, suppresses precipitation of the hydrides. This leads the zirconium matrix to have a higher dissolved hydrogen concentration upon cooling as opposed to the equilibrium hydrogen concentration upon heating. That is why the TSSP becomes larger than the TSSD as shown in Fig. 1.

When the Zr-2.5Nb compact tension (CT) specimen with a hydrogen concentration in excess of 60 ppm H is heated up to a peak temperature of 310 ^{o}C in a thermal cycle, it dissolves hydrogen whose concentration corresponds to the A point (as shown in Fig. 2) following the TSSD line. On cool-down to the test temperatures or 250 ^{o}C from the peak temperature, the Zr-2.5Nb specimen keeps all the hydrogen dissolved without precipitating any hydrides out of the zirconium matrix hydrostatically compressed by cooling. This corresponds to a case where the TSSD at the peak temperature is less than the TSSP at the test temperature. It leads the specimen to have the supersaturation of the dissolved hydrogen because the equilibrium hydrogen concentration that the Zr-2.5Nb specimen can dissolve is equal to the C point of Fig. 1,
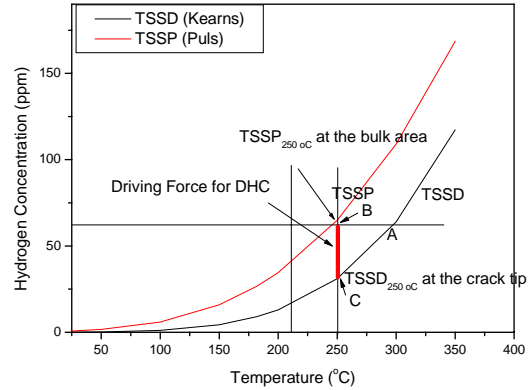

Fig. 1. The TSS lines of hydrogen during a thermal cycle which the Zr-2.5Nb tubes are subjected during DHC tests. The driving force for DHC is a concentration gradient of hydrogen of hydrogen accompanied by the precipitation of hydrides at the crack tip under a tensile stress:
TSSP $_{at the bulk area}$ $-$TSSD $_{at the crack tip}$ at the test temperatures.

following the TSSD line. The amount of supersaturation of hydrogen, thus, corresponds to the distance BC as shown in Fig. 1. In general, the maximum supersaturated hydrogen concentration that the zirconium matrix can have in the thermal cycle will be TSSP-TSSD at any temperatures when the specimen is charged to a hydrogen concentration that is sufficient to exceed the TSSP at test temperatures. When a tensile stress is applied to Zr-2.5Nb CT specimens with a crack maintaining the supersaturated concentration of the dissolved hydrogen, the work energy given by the applied tensile stress will compensate for part of the increased strain energy by the precipitating hydrides with a larger volume. Hence, this will facilitates precipitation of the hydrides only at the crack tip. This causes the supersaturated hydrogen concentration at the crack tip to be reduced ultimately to the equilibrium hydrogen concentration or TSSD. In other words, the tensile stress applied at the crack tip will act to trigger nucleation of the hydrides only at the crack tip, thus decreasing the supersaturated hydrogen concentration to the TSSD at the test temperature or the C point as shown in Fig. 2. In contrast, the bulk region, which is subjected to small tensile stress, still maintains the supersaturation of hydrogen. This consequently leads to the development of a difference in the hydrogen concentration or ΔC between the crack tip and the bulk region corresponding to the distance BC, as shown in Fig. 1. Therefore, there arises a driving force for hydrogen to move from the bulk region to the crack tip. This difference in the hydrogen concentration or the amount of supersaturation of hydrogen (ΔC) is a driving force for the DHC. It should be noted that the maximum hydrogen concentration difference, ΔC_{max} is the TSSP-TSSD at any test temperatures as shown in Fig. 1. On the contrary, if the charged hydrogen concentration is less than ΔC_{max} (=TSSP-TSSD) at the test temperature, then the DHCV will be greatly affected with the hydrogen concentration. In essence, the driving force for the DHC is a hysteresis of the TSS on heating and cooling..

A model experiment was conducted to demonstrate the feasibility of the new DHC model proposed where the effect of plastic deformation on precipitation of reoriented hydrides and their effect on DHC susceptibility were investigated during a thermal cycle treatment of a Zr-2.5Nb tube. Furthermore, the effect of the supersaturated hydrogen concentration on the DHCV was also investigated using the Zr-2.5Nb compact tension specimens with the hydrogen concentration changing from 12 to 100 ppm.

3. Results

The feasibility of the new DHC model proposed here can be proven if the applied tensile stress facilitates precipitation of the hydrides from zirconium with supersaturated hydrogen, thereby causing a hydrogen concentration gradient. To this end, a model experiment was conducted where the same tensile stress corresponding to 18.4 MPa√m was applied to the CB specimens at different times in a thermal cycle as shown in Fig. 2: first, at the beginning of the cycle or at room temperature (A point); second, at the end of a 50 hour-hold at the peak temperature (B point) and third, at the beginning of the test temperature (C point). It should be noted that the stress intensity factor of 18.4 MPa√m (termed K) is calculated based on the assumption that a notch with 0.05 mm radius in the CB acts as a sharp crack. With the K applied at the points A or B, the reoriented hydrides precipitated over almost the whole cross-section and at a small area near the crack tip, respectively, as shown in Figs. 2b and 3c. With the same K applied at the test temperature of 250 °C, however, slight precipitation of reoriented hydrides was observed, as shown in Fig. 2d..

The model experiment definitively demonstrates that the applied tensile stress facilitates precipitation of the reoriented hydrides in the deformed regions whose size depends upon when to apply the tensile stress during the thermal cycle. In contrast, with the same tensile stress applied at the test temperature, the relative small plastic deformation of the Zr-2.5Nb matrix suppressed precipitation of the reoriented hydrides somewhere else but the crack tip, as shown in Fig. 2. Surprisingly, the DHC crack did not grow in the specimens with the reoriented hydrides having precipitated all over the whole cross-section on cooling (Fig. 2b) but grew only in the specimen with a few reoriented hydrides precipitated at the crack tip (Fig. 2d). These results cannot be understood with the old DHC model where the tensile stress gradient is the driving force for the DHC. They are also in conflict with the current understanding that reoriented hydrides at the crack tip would facilitate growth of the DHC crack [3].

4. Conclusion

For the first time, we propose a new DHC model where a driving force for DHC of zirconium alloys is the supersaturated hydrogen concentration or ΔC resulting from hysteresis of the terminal solid solubility of hydrogen in zirconium upon heating and cooling. Experimental evidence to the feasibility of the new DHC model was provided through the model experiments: the applied stress promoted precipitation of the reoriented hydrides in the plastic zone, no DHC occurred in the absence of the supersaturation of hydrogen resulting from the reoriented hydrides precipitated all over the cross-section on cooling, and the DHCV of the Zr-2.5Nb tube increased with the ΔC and leveled off to a
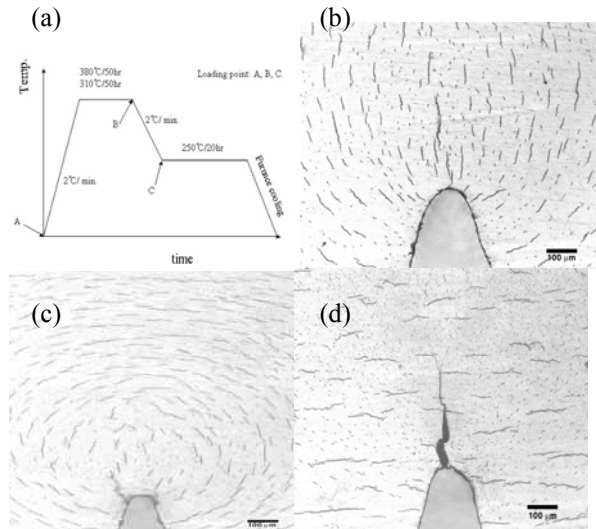

Fig. 2. (a) Thermal cycle treatment to which the Zr-2.5Nb cantilever beam specimens were subjected during DHC tests with the stress intensity factor of 18.4 MPa√m, (b,c.d) Reorientation of hydrides in the Zr-2.5Nb tube with time of application of the stress intensity factor: (b) at point A, (c) at point B and (d) at point C.

constant at the ΔC in excess of TSSP-TSSD at the test temperature. The new DHC model proposed here comprehends the constant DHCV independent of the K accounting for the facts that the ΔC becomes independent of the K and the plastic zone size Δs is governed by the yield strength and the threshold stress intensity factor over which the hydrides precipitated at the crack tip fracture, initiating the DHC.

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