Roles of intergranular δ-hydrides in the failure of hydrided Zr alloys

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Abstract

Roles of intergranular δ-hydrides in the failure of hydrided Zr alloys are studied based on the analysis of the link-up of microcracks produced due to the hydride rupture and the thermodynamic modelling of the stress-induced formation of inter- and intra-granular hydrides. Our results show that the intergranular hydrides may be more deleterious to the ductility than the intragranular ones and the fracture mechanism of the hydrided Zr alloys is related to the grain-boundary structure, the orientation of the Zr grains along the grain boundaries and the applied stress.

1. Introduction

Due to the embrittlement of Zr hydrides at low temperature, a transition from the ductile to the brittle fracture occurs when the hydrides precipitate and form a network configuration [1]. Although the initiation of fracture from hydrides has been the subject of intensive research, currently available work is mainly concerned with the intragranular hydrides, and nearly no attention has been paid on the intergranular ones. Some works have shown that the intergranular hydrides play a more important role than the intragranular ones in the hydride-related degradation of Zr alloys [2,3]. In this paper, a thermodynamic approach is proposed to analyze the fracture behaviour of the hydrided Zr alloys by simultaneously considering the inter- and intra-granular hydrides.

2. Rupture of intergranular hydrides

The strain inhomogeneity between the matrix and the hydride during deformation can produce an internal stress (σ_I) imposing on the hydrides and cause the hydride rupture. The σ_I may be calculated by [4]

$$\sigma_I = \lambda E_P \Delta\varepsilon \tag{1}$$

where λ is a constant, $\Delta\varepsilon = \varepsilon_{\mathrm{Zr}} - \varepsilon_{\mathrm{hyr}}$ with $\varepsilon_{\mathrm{Zr}}$ and $\varepsilon_{\mathrm{hyr}}$ being the strains of Zr matrix and hydrides, respectively, and E_p is the plastic equivalent Young's modulus of Zr matrix. The strain rates of Zr matrix ($d\varepsilon_{\mathrm{Zr}}/dt$) is related to the slip systems [5]

$$d\varepsilon_{Zr}/dt = \gamma\left(\Gamma_{yield}/\mu\right)^2 \exp\left\{-F_0/kT\left[1-\left(\Gamma/\Gamma_a\right)^p\right]^q\right\} \tag{2}$$

where γ is a constant, μ is the elastic shear modulus, Γ_{yield} is the yield shear stress, Γ and Γ_a are the driving (tangential) stress in the slip system and the peierls stress at which dislocation is mobilized without the assistance of thermal activation, respectively, F_0 is the activation energy required for a dislocation to move past the discrete obstacles, and p and q are the constants. Whether a slip system is activated depends on whether the resolved shear stress in the slip system exceeds the critical resolved shear stress. The δ-hydride formation in Zr matrix prefers certain crystallographic planes, such as frequently reported (0001) plane [6]. For intergranular hydrides, our studies show that the crystallographic relationship of $(0001)_{\alpha\text{-Zr}}//\{111\}_{\delta\text{-ZrH1.66}}$ is still valid, but only exists between hydrides and one of the bounding Zr grains, as shown in Fig. 1 [6]

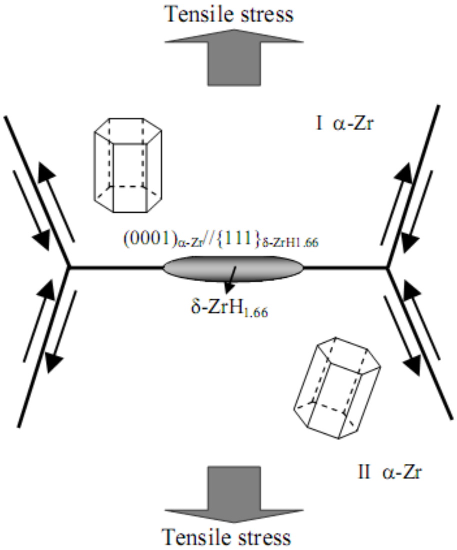

Fig. 1. The preferred nucleation sites of the intergranular δ-hydrides and the effects of strain inhomogeneity between the matrix and the hydride on the hydride rupture.

If the slip system of Zr matrix is coincident with that of hydrides, the dislocations can go through from Zr matrix to hydrides and consequently the value of $\Delta\varepsilon$ is small. However, for intergranular hydrides, due to different crystallographic orientations of two adjacent Zr grains, even if the slip system of intergranular hydride coincides with that one grain it cannot generally coincide with that of the other. Intergranular hydrides are therefore submitted to higher strain incompatibilities and stresses, as a result of which the intergranular hydrides break more easily.

3. Link-up of microcracks produced by hydride rupture

Under the tensile stress, the microcracks produced in hydrides could propagate into the Zr matrix. The ductile fracture of the Zr matrix starts when the local strain reaches a critical value (ε_c). For closely spaced hydride plates, the pileup of the local strain fields in the front of the tips of two adjacent microcracks can accelerate the fracture of Zr matrix, as shown in Fig. 2.

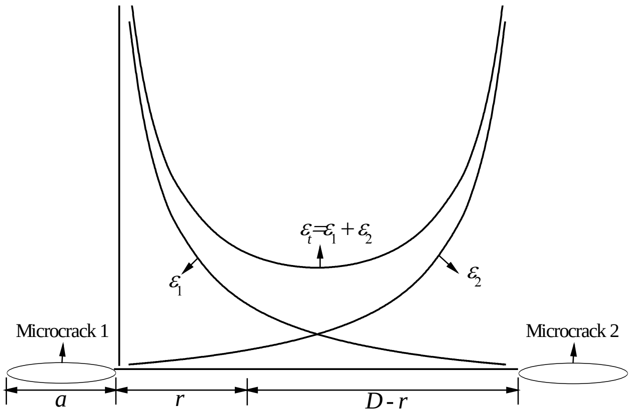

Fig. 2. Geometrical description of the pileup of the local strain fields between the two adjacent microcracks.

The local stress distribution (σ) in a distance (r) from the microcrack tip may be calculated using HRR-field model [7]

$$\sigma = \sigma_y \left\{ \left[K_1 \left(1-\nu^2\right) \right] / \alpha \sigma_y^2 I r \right\}^{1/1+n} \overline{\omega(\theta)} \tag{3}$$

where ν is the Poisson's ratio, n and α are material constants, σ_y is yield stress and K_1 is the stress intensity factor, which is written as $K_I = \sigma_p(\pi a/2)^{1/2}$, in which a is the crack length and σ_P is the applied stress. For the hydrided Zr alloys, a may be regarded as the size of hydrides. According to the Osgood-Ramberg relationship between the stress σ and the strain ε, we have

$$\frac{\varepsilon}{\varepsilon_y} = \alpha \left[\frac{\sigma}{\sigma_y} \right]^n = \alpha \left[\frac{\sigma_p (\pi a/2)^{1/2} \left(1-\nu^2\right)}{\alpha \sigma_y^2 I r} \right]^{n/1+n} \left[\overline{\omega(\theta)} \right]^n \tag{4}$$

where ε_y is yield strain. For the crack propagation in the crack tip, the tensile stress normal to the crack plane near the tip is the most important component. In this regard, $\overline{\omega(\theta)} = 1$ when $\theta = 0$. In order to determine the material constants of n and α, Osgood-Ramberg parameters were fitted to the stress-strain data obtained from the tensile tests of Zr-2.5Nb alloy [4]. The results show that its mechanical behavior is close to that of elastic-perfectly plastic materials. Puls suggested that $n = 100$ and $\alpha = 1\times10^{-5}$ [4]. As a result, the approximation of $n/(1+n) \rightarrow 1$ may be acceptable. Due to the pile-up effect of the strain fields in the front of the crack tips, the total strain between the two (ε_t) is

$$\varepsilon_t = \left[\alpha\, \varepsilon_y \sigma_p (\pi a/2)^{1/2} \left(1-\nu^2\right) / \left(\alpha\, \sigma_y^2 I\right) \right] \left[1/r + 1/(D-r) \right] \tag{5}$$

where D is the in-plane distance between the two adjacent hydrides. The strain concentration can cause a complete failure of the ligament connecting two interacting microcracks when $\varepsilon_t > \varepsilon_c$ at $r = D/2$. The critical condition for the linkage of two adjacent microcracks through the Zr matrix is thus

$$4 \alpha \varepsilon_y \sigma_{p,c} (\pi a_c/2)^{1/2} \left(1-\nu^2\right) / \left(\alpha \sigma_y^2 I D_c\right) = \varepsilon_c \tag{6}$$

where $\sigma_{P,c}$, a_c and D_c are their corresponding critical values. In general, the critical fracture strain required for cleavage at the GBs ($\varepsilon_{c,GB}$) is much smaller than that in the grains ($\varepsilon_{c,G}$) because of more weaken atomic bonding. Therefore, hydride formation in the GBs is much more likely to cause the full-scale failure of matrix.

4. Effects of applied tensile stress on fracture mechanism

Above results show that hydride distribution in Zr alloys may affect the fracture mechanism. The site preference of hydrides depends on its nucleation process in the different sites. Based on the model developed by us, the ratio of hydride nucleation at the GBs (J_{GB}^*) to that in the grain ($J_{\mathrm{int}ra}^*$) may be estimated by [6]

$$J^*_{GB}\big/J^*_{\mathrm{int}\,ra} = \left(3\rho\Lambda/d\right)\exp\left[-\left(\Delta G^*_{tens,GB} - \Delta G^*_{tens,\mathrm{int}\,ra} - 2r_0^2\tau_{\alpha\alpha}\right)/\,kT\right] \tag{7}$$

where ρ is the GB thickness, d is the grain size, Λ is the probability of habit plane lying on the GBs, r_0 is the nearest interatomic distance, and τ_{aa} is the GB energy, $\Delta G^*_{tens,GB}$ and $\Delta G^*_{tens,\mathrm{int}\,ra}$ are the critical nucleation energies of the intergranular and the intragranular hydrides, respectively. The $\Delta G^*_{tens,GB}$ under tensile stress (σ_p) may be calculated by [6]

$$\Delta G^*_{tens,GB} = \frac{4\pi\tau^3_{\alpha\delta}\left[2-3\left(\tau_{\alpha\alpha,0}+\sigma_p\kappa\rho cons\varphi\right)/\tau_{\alpha\delta}+\left(\tau_{\alpha\alpha,0}+\sigma_p\kappa\rho cons\varphi\right)^3/4\tau^3_{\alpha\delta}+3\tau^c_{\alpha\delta}/\tau_{\alpha\delta}-\left(\tau^c_{\alpha\delta}\right)^3/\tau^3_{\alpha\delta}\right]}{3\left[-\Delta G_{chem}-\left(x/\bar{\upsilon}_{hyd}\right)\left[\left(\sigma_p cons\varphi\right)/3\right]\bar{\upsilon}_H-\left(\sigma_p cons\varphi\right)\chi+\Delta G^{GB}_{strain}\right]^2} \tag{8}$$

where ΔG_{chem} is the absolute value of chemical free energy of transformation per unit volume, ΔG^{GB}_{strain} is the strain energy per unit volume for hydride formation at the GBs. $\bar{\upsilon}_{hyd}$ is the molar volume of hydrides of composition ZrH_x, with $x = 1.66$ for δ phase, and $\bar{\upsilon}_H$ is the molar volume of hydrogen in Zr, φ is the angle between the tensile stress axis and the normal to the hydride plate (or the GB plane), χ is the Zr matrix-hydride misfit strain, $\tau_{\alpha\delta}$ is the disordered interfacial energy and $\tau^c_{\alpha\delta}$ is the coherent interfacial energy, $\tau_{\alpha\alpha,0}$ is the GB energy without tensile load and κ is the local strain caused by tensile stress in the GB region. For the intragranular δ-hydride, the critical nucleation energy under tensile stress ($\Delta G^*_{tens,\mathrm{int}\,ra}$) is calculated using Puls' model [8]

$$\Delta G^*_{tens,\mathrm{int}\,ra} = \left(18\pi\tau^c_{\alpha\delta}\tau^2_{\alpha\delta}\right)\Big/\left[-\Delta G_{chem}-\left(x/\bar{\upsilon}_{hyd}\right)\left[\left(\sigma_p cons\varphi\right)/3\right]\bar{\upsilon}_H-\left(\sigma_p cons\varphi\right)\chi+\Delta G^{GB}_{strain}\right]^2 \tag{9}$$

For $ZrH_{1.66}$ hydrides, $\Delta G_{chem} = 4.02\times10^8$ J/m^3, $\bar{\upsilon}_{hyd} = 16.3\times10^{-6}$ m^3/mol, $\bar{\upsilon}_H = 1.67\times10^{-6}$ m^3/mol, $\chi = 0.0458$, $\kappa = 0.003$, $\rho = 5.146\times10^{-10}$ m, $\Delta G^{GB}_{strain} = 2.724\times10^8$ J/m^3, $\tau_{\alpha\delta} = 0.5$

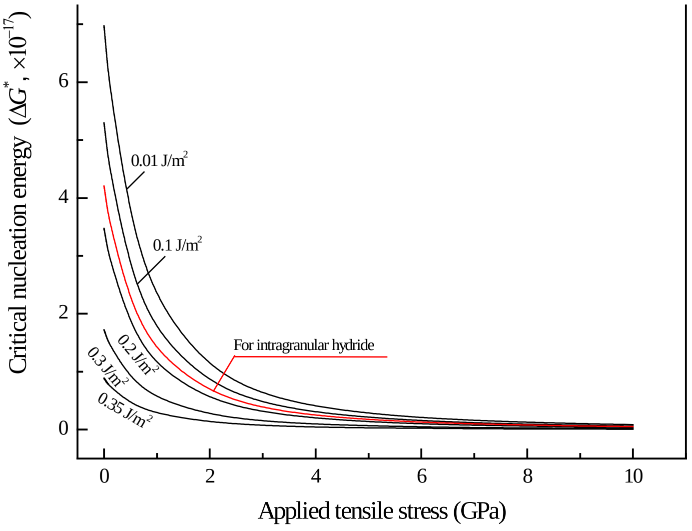

Fig. 3. Changes of critical nucleation energy of inter- and intra-granular hydrides with the applied tensile stress and the GB energy.

J/m^2 and $\tau_{\alpha\delta}^{c}$ = 0.05 J/m^2. In general, the hydride platelets always tend to form perpendicularly to the stress axis, i.e., $\varphi = 90^\circ$. The calculated $\Delta G^*_{tens,GB}$ is shown in Fig. 3. The result of $\Delta G^*_{tens,\mathrm{int}ra}$ is also given in the same figure for comparison. It is seen that the tensile stress can substantially lowers the critical nucleation energy of hydrides and results in the decrease in the difference of the critical nucleation energies between $\Delta G^*_{tens,GB}$ and $\Delta G^*_{tens,\mathrm{int}ra}$. As a result, the ratio of $J^*_{GB} / J^*_{\mathrm{int}ra}$ will decrease with increasing the applied tensile stress, as indicated from Eq. (7). This means that hydrides tend to simultaneously precipitate at the GBs and in the grains with increasing tensile stress. That is to say, under the high load, the failure of the hydrided Zr alloys tends to be a complicated behavior combining the transgranular and the intergranular fracture.

5. Conclusion

(1) Due to the different crystallographic orientations of two adjacent Zr grains and strain inhomogeneity between the matrix and the hydride, intergranular hydrides are submitted to a higher internal stress, and therefore break more easily.

(2) The fracture in Zr matrix ligament between the intergranular hydride microcracks leads to the cracks propagating along the GBs (intergranular fracture). The intergranular hydrides can cause a larger degradation of ductility.

(3) Applied tensile stress may substantially change the site preference of hydride formation. Under the high load, the failure of the hydrided Zr alloys is a combination effect of the transgranular and the intergranular fracture.

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