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Modeling of hydrogen diffusion process at a blunt notch in zirconium

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Abstract: The two-dimensional diffusion of interstitial hydrogen atoms in zirconium in a non-uniform stress field was simulated using the phase-field method. The interaction between hydrogen interstitials and the stress field was described by Khachaturyan's elastic theory. The Cahn-Hilliard diffusion equation was then solved by an explicit finite difference method. The result shows that hydrogen atoms diffuse to the high-tensile hydrostatic region near the tip of the notch. The content of hydrogen near the tip of the notch increases by 13%, while the stress distribution caused by hydrogen interstitials around the notch is modified by only 0.7%.

Key words: phase-field; hydrogen; diffusion; non-uniform applied stress; zirconium

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1 Introduction

Zirconium and its alloys are structural materials in the nuclear power industry. These alloys can gradually pick up hydrogen from a hot water environment through a slow corrosion process. It is well known that hydrogen is particularly attractive to high-tensile regions such as a crack or a notch tip. When the content of hydrogen in the alloys exceeds the terminal solid solubility (TSS), zirconium hydrides will form. This may cause the alloys to become susceptible to a crack initiation and propagation process called the delayed hydride cracking (DHC), or other forms of hydride embrittlement.

Because of the difficulty and high costs of an in-situ observation of the dynamic process of hydrogen diffusion and hydride growth in irradiated materials, theoretical modeling is an important means to investigate the DHC process. Dutton and Puls [1] developed a one-dimensional, steady-state diffusion model for DHC. In this model, it was assumed that the stress field around the crack tip has cylindrical symmetry and that the hydrogen diffusion has reached a steady state throughout the whole field. This model has provided explanations for some significant features of the DHC process, but cannot handle the time-dependent diffusion effect. Metzger *et al.* [2] developed a finite-element method to deal with the time-dependent 2D or 3D diffusion problem in DHC. This method has been used to examine hydrogen diffusion at a notch under temperature cycling. Shi *et al.* [3] extended Dutton and Puls's model to time-dependent situations and incorporated a fracture criterion into the model. In all of these models, the morphology of hydride precipitates based on simplified assumptions, such as a single hydride plate on a crack plane and the interactions between hydrogen atoms or hydrides were neglected. It is well known that interstitial hydrogen atoms can cause a local lattice distortion. This lattice distortion may induce hydrogen-hydrogen interactions as well as modifications to the stress distribution around a notch. Therefore, the investigation of the hydrogen diffusion behavior in a non-uniform stress area and considering interaction between the hydrogen atoms is the essential step for studying DHC.

The phase-field method has become a powerful tool in recent years in modeling the diffusion and phase transformation process under uniform and non-uniform applied stress. The morphology of hydride precipitation under uniform applied stress has already been studied by the phase-field method [4-6]. However, the most dangerous situation is the precipitation

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of hydrides under non-uniform applied stress, such as at a flaw tip. Because the phase-field method can take all the interactions into account and predict the redistribution of hydrogen as a function of time and other environmental parameters, a study of a hydrogen diffusion process near a notch tip by using the phase-field method was reported in this paper.

2 Numerical method

2.1 System **description and calculation of applied stress field**

To investigate the hydrogen diffusion near a notch tip, a system was constructed as follows to mimic cantilever test conditions. The sample is a zirconium rectangular bar containing uniformly distributed diluted hydrogen. As shown in **figure 1,** the sample is 38 mm long and 5 mm wide. A notch with a flank angle of 45° and a depth of 1.0 mm was cut at the center of one edge. The root radius of the notch tip is 0.3 mm. The yield strength of the specimen was assumed to be about 850 MPa at 250°C (the value for fully irradiated Zr-2.5Nb alloys) [7]. The left-hand side of the specimen was held still, and a constant weight of 35 N and 50 N was applied to the right-hand side respectively. In this work, a commercial finite element method (FEM) software NASTRAN® was used to calculate the stress distribution around the notch. The average mesh size in the area around the notch is 0.03 mm. The resulting maximum stress σ_{xx} near the notch tip is about 670 MPa for the 50 N load, which is still within the elastic regime. The stress distributions are shown in **figure 2.** The hydrostatic stress distribution along the centerline of the notch is given in **figure 3,** showing a high hydrostatic stress zone in front of the notch tip. The maximum hydrostatic stress is reached in front of the notch tip. The stress concentration near the notch tip is the driving force for hydrogen diffusion, which will cause the redistribution of hydrogen atoms. The stress distribution calculated by NASTRAN® was then mapped into a uniform grid by interpolation and was used as the applied stress in hydrogen diffusion analysis.

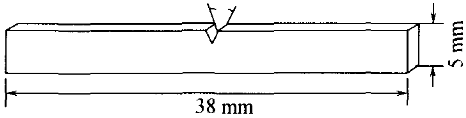

Figure 1 Dimension of the cantilever.

2.2 **Cahn-Hilliard equation and the chemical potential of hydrogen**

To simulate the hydrogen diffusion process in a zirconium specimen with a notch, the compositional field *c(r,t),* the atomic fraction of hydrogen atoms, was adopted as the phase-field parameter. The initial condition for *c(r,t)* is $c(r,0)=c_0$. The governing equation of *c(r,t)* for the diffusion process is the Cahn-Hilliard equation [8],

$$\frac{\partial c}{\partial t}=\nabla\cdot(M\nabla\mu) \tag{1}$$

where M is the mobility and μ is the chemical potential of hydrogen. The mobility of hydrogen is defined as

$$M = Dc(\mathbf{r},t)/RT,$$

where D is the diffusivity of hydrogen in zirconium, R is the gas constant and T the thermodynamic temperature. If D and T are not a function of locations, then equation (1) can be further expended to

$$\frac{\partial c}{\partial t}=\frac{D}{RT}[c\nabla^2\mu+\nabla c\cdot\nabla\mu] \tag{2}$$

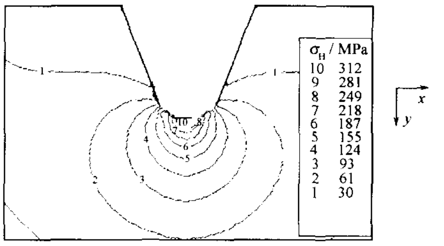

Figure 2 Hydrostatic stress around the notch caused by the 50 N applied load at the right-hand side of the cantilever.

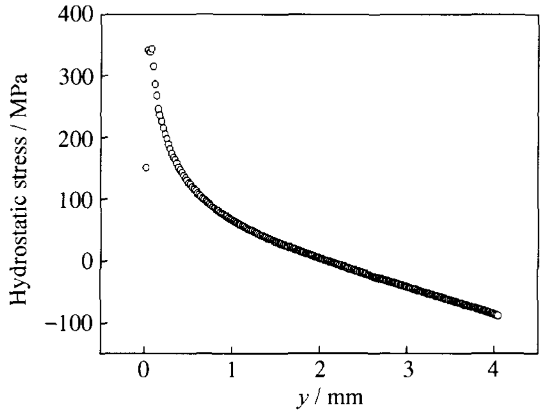

Figure 3 Hydrostatic stress caused by the 50 N applied load along the centerline of the notch.

The chemical potential of hydrogen is defined by

$$\mu=\frac{\partial E_G}{\partial n_{mH}}=\frac{\partial E_G}{n_m\partial c} \tag{3}$$

where E_G is the Gibbs free energy, n_{mH} represents the amount of substance of hydrogen atoms, and n_m is the amount of substance of all atoms including zirconium. The Gibbs free energy for hydrogen in a solid solution is defined by

$$E_G = E + W - TS \tag{4}$$

where E is the internal energy that includes mainly two parts: a chemical part (E_c) related to bonding properties between the hydrogen and metal matrix, and another part (E_e) related to the elastic distortion energy of the lattice due to the presence of hydrogen interstitials without externally applied stress. W is the work done by external forces. Finally, S is the entropy of the system, which is the sum of the entropy of vibration (S_v) and the entropy of mixing (S_m). Therefore, equation (4) becomes

$$E_G = E_c + E_e + W - T(S_v + S_m) \tag{5}$$

Using lower cases of the letters to represent the quantities for 1 mol of hydrogen, and assuming a diluted solution, the Gibbs free energy can be written as

$$E_G = n_{mH}(e_c + e_e + w - Ts_v) - TS_m \tag{6}$$

where S_m needs a special treatment because it involves the mixing of hydrogen with zirconium atoms. The result is

$$S_m = -n_m R\{c(\boldsymbol{r},t)\ln[c(\boldsymbol{r},t)] + [1-c(\boldsymbol{r},t)]\ln[1-c(\boldsymbol{r},t)]\} \tag{7}$$

From equation (3), the chemical potential can be found as

$$\mu = e_c + e_e + w - Ts_v + RT\ln\frac{c(r,t)}{1-c(r,t)} =$$

$$\mu_0 + e_e + w + RT\ln\frac{c(r,t)}{1-c(r,t)} \tag{8}$$

where μ_0 is the combination of e_c and $-Ts_v$, which is not a function of r, based on the assumptions of uniform temperature and a diluted solution. Therefore, μ_0 will not contribute to the solution of the Cahn-Hilliard equation. The terms e_e and w are related to the elastic energy of hydrogen interstitials under externally applied stress, and will be studied in the next section.

2.3 Elastic energy of hydrogen interstitials

Assuming a linear elastic system, the total elastic energy of hydrogen interstitials in zirconium lattice under externally applied stress by analyzing the total elastic strain associated with hydrogen interstitials as well as the applied stress can be studied,

$$\varepsilon_{ij}^{el}(\boldsymbol{r}) = \varepsilon_{ij}(\boldsymbol{r}) - \varepsilon_{ij}^{0}(\boldsymbol{r}) + \varepsilon_{ij}^{a}(\boldsymbol{r}) \tag{9}$$

where $\varepsilon_{ij}(r)$ is the total strain of the system without externally applied stress, $\varepsilon_{ij}^{0}(r)$ is the local stress-free strain caused by hydrogen interstitials and $\varepsilon_{ij}^{a}(r)$ is the strain created by the applied stress. The local elastic stress-free strain can be further expanded in terms of the local hydrogen composition change $\delta c(r)$, where $\delta c(r)=c(r)-c_m$. We have

$$\varepsilon_{ij}^{0}(\boldsymbol{r}) = \varepsilon_{ij}^{c}\delta c(\boldsymbol{r}) \tag{10}$$

where ε_{ij}^{c} is the stress-free strain caused by each hydrogen atom. The elastic stress field is then given by

$$\sigma_{ij}^{el} = C_{ijkl}\varepsilon_{kl}^{el}(\boldsymbol{r}) = C_{ijkl}[\varepsilon_{kl}(\boldsymbol{r}) - \varepsilon_{kl}^{0}(\boldsymbol{r}) + \varepsilon_{kl}^{a}(\boldsymbol{r})] \tag{11}$$

where C_{ijkl} is the elastic constant of the Zr lattice.

The force equilibrium condition will give

$$\frac{\partial\sigma_{ij}^{el}}{\partial r_j} = 0 \tag{12}$$

According to reference [9], the total strain $\varepsilon_{ij}(r)$ may be represented as the sum of the homogeneous and heterogeneous strains:

$$\varepsilon_{ij}(\boldsymbol{r}) = \bar{\varepsilon}_{ij} + \delta\varepsilon_{ij}(\boldsymbol{r}) \tag{13}$$

where the homogeneous strain $\bar{\varepsilon}_{ij}$ is defined so that

$$\int_V \delta\varepsilon_{ij}(\boldsymbol{r})\mathrm{d}^3\boldsymbol{r} = 0 \tag{14}$$

The homogeneous strain is the uniform macroscopic strain that contributes to the macroscopic shape and volume change, while the heterogeneous strain has no macroscopic effects. The heterogeneous strain can be expressed in terms of heterogeneous displacement,

$$\delta\varepsilon_{kl}(\boldsymbol{r}) = \frac{1}{2}\left[\frac{\partial u_k}{\partial r_l} + \frac{\partial u_l}{\partial r_k}\right] \tag{15}$$

where u_k is the displacement along the k axis. Substituting (10), (11), (13) and (15) into the mechanical equilibrium condition (12), we have

$$C_{ijkl}\frac{\partial^2 u_k(\boldsymbol{r})}{\partial r_j\partial r_l} = C_{ijkl}\left[\varepsilon_{kl}^{c}\frac{\partial\delta c(\boldsymbol{r})}{\partial r_j} - \frac{\partial\varepsilon_{kl}^{a}(\boldsymbol{r})}{\partial r_j}\right] \tag{16}$$

Solving the above equation in the Fourier space, we get

$$u_k(\boldsymbol{g}) = -iG_{ik}(\boldsymbol{g})[\sigma_{ij}^{c}\delta c(\boldsymbol{g}) - \sigma_{ij}^{a}(\boldsymbol{g})]g_j \tag{17}$$

where g is a reciprocal lattice vector, g_j is the *jth* component of $\boldsymbol{g}$, $\sigma_{ij}^{c} = C_{ijkl}\varepsilon_{kl}^{c}$, and $\sigma_{ij}^{a}(\boldsymbol{g})$ is the applied stress. $G^{-1}(\boldsymbol{g})_{ik} = C_{ijkl}g_j g_l = g^2 C_{ijkl}n_j n_l = g^2\Omega_{ik}^{-1}(\boldsymbol{n})$. For an elastically isotropic system,,

$$\Omega_{ij}(n) = \frac{\delta_{ij}}{G} - \frac{n_i n_j}{2G(1-v)} \tag{18}$$

where G is the shear modulus and v is the Possion's ratio, n=*glg, Fig)* is the Fourier transformation of *F(r)*. The elastic energy density at the site r is given by

$$e_{el} = \frac{1}{2}C_{ijkl}\varepsilon_{ij}^{el}(\boldsymbol{r})\varepsilon_{kl}^{el}(\boldsymbol{r}) \tag{19}$$

Considering the derivations from (9) to (19), the elastic energy can be expressed as

$$E_{\mathrm{el}} = \int \frac{1}{2} C_{ijkl} \varepsilon^{\mathrm{a}}_{ij}(\boldsymbol{r}) \varepsilon^{\mathrm{a}}_{ij}(\boldsymbol{r}) \mathrm{d}V - \int C_{ijkl} \varepsilon^{\mathrm{c}}_{ij} \delta c(\boldsymbol{r}) \varepsilon^{\mathrm{a}}_{kl}(\boldsymbol{r}) \mathrm{d}V +$$

$$\int \frac{1}{2} C_{ijkl} \varepsilon^{\mathrm{c}}_{ij} \varepsilon^{\mathrm{c}}_{kl} [(\delta c(\boldsymbol{r})]^2 \mathrm{d}V -$$

$$\int \frac{\mathrm{d}^3 \boldsymbol{g}}{(2\pi)^3} n_i \sigma'_{ij}(\boldsymbol{g}) \Omega_{jk}(\boldsymbol{n}) (\sigma'_{kl}(\boldsymbol{g}))^* n_l \tag{20}$$

where

$$\sigma'_{ij}(\boldsymbol{g}) = \sigma^{\mathrm{c}}_{ij} \delta c(\boldsymbol{g}) - \sigma^{\mathrm{a}}_{ij}(\boldsymbol{g}) \tag{21}$$

The expression (20), in fact, represents both the elastic distortion energy E_e and the interaction energy W in equation (5). We have

$$\mu = \mu_0 - V_{\mathrm{mol}} C_{ijkl} \varepsilon^{\mathrm{c}}_{ij} \varepsilon^{\mathrm{a}}_{kl} + V_{\mathrm{mol}} C_{ijkl} \varepsilon^{\mathrm{c}}_{ij} \varepsilon^{\mathrm{c}}_{kl} \delta c(\boldsymbol{r}) +$$

$$\left[\int \frac{\mathrm{d}^3 \boldsymbol{g}}{(2\pi)^3} n_i \sigma^{\mathrm{c}}_{ij}(\boldsymbol{g}) \Omega_{jk}(\boldsymbol{n}) (\sigma^{\mathrm{a}}_{kl}(\boldsymbol{g}))^* n_l \right]_{\mathrm{r}} -$$

$$\left[\int \frac{d^3 \boldsymbol{g}}{(2\pi)^3} n_i \sigma^{c}_{ij}(\boldsymbol{g}) \Omega_{jk}(\boldsymbol{n}) (\sigma^{c}_{kl}(\boldsymbol{g}))^* n_l \right]_{\mathrm{r}} +$$

$$RT\{\ln[c(\boldsymbol{r},t)] - \ln[1 - c(\boldsymbol{r},t)]\} \tag{22}$$

where V_{mol} is the mole volume of zirconium and $[...]_{\mathrm{r}}$ represents the backward Fourier transformation of quantities in [...]. According to the expression (22), the chemical potential of hydrogen is a function of both hydrogen composition and stress. The second and fourth term of the expression (22) represent the chemical potential caused by the interaction between the applied stress and the strain field of hydrogen. The fourth term reflects the influence of the applied stress at the site r on the strain caused by hydrogen at another site r',and it is a smaller amount than the second term. The third and fifth terms represent the elastic interaction between the hydrogen atoms. They are at least one order of magnitude smaller than the second term due to the diluted hydrogen composition condition.

The Cahn-Hilliard equation was solved by an explicit Euler finite-difference method. The system is divided into a 512×512 uniform Cartesian grid, with the distance between the nearest grid point Δx or Δy being along the x or y direction respectively, $\Delta x = \Delta y = h$. In the finite-difference method, the Cahn-Hilliard equation (2) takes the form of

$$c^{n+1}_{i,j} = c^{n}_{i,j} + \frac{D\Delta t}{RT} \left\{ \frac{1}{\Delta x^2} c^{n}_{i,j} \cdot [(\mu_{i+1,j} + \mu_{i-1,j} + \mu_{i,j+1} + \right.$$

$$\mu_{i,j-1} - 4\mu_{i,j})] + \left(\frac{1}{4\Delta x^2} \right) [(c^{n}_{i+1,j} - c^{n}_{i-1,j}) \times$$

$$\left. (\mu_{i+1,j} - \mu_{i-1,j}) + (c^{n}_{i,j+1} - c^{n}_{i,j-1})(\mu_{i,j+1} - \mu_{i,j-1})] \right\} \tag{23}$$

The hydrogen flux is equal to

$$J = -M \nabla \mu \tag{24}$$

where M is the mobility of hydrogen atoms. The boundary condition at the surface of the notch is that the hydrogen flux across the boundary is zero. Since hydrogen diffusion in the area around the notch are mainly concerned with, to simplify the calculation, the other boundaries are treated as periodic conditions. Considering these boundary conditions and numerically solving the Cahn-Hilliard equation, the temporal and spatial evolution of hydrogen content is obtained.

3 Simulation results and discussion

The parameters used in the calculations are given in following: the initial hydrogen concentration c_0=0.6%; the diffusivity of H in Zr $D_H = 5.468 \times 10^{-7} e^{-45293/RT}$ m^2/s [3]; the mole volume of Zr $V_{\mathrm{mol}} = 1.4 \times 10^{-5}$ m^3/mol [10]; the Young's modulus of Zr E=81.5 GPa at T=250°C [7]; the Possion's ratio, v=0.33 at T=250°C [7]; the strain ε^c caused by a hydrogen atom (hydrogen isotope, deuterium) in Zr, $\varepsilon_{11}{}^{c} = \varepsilon_{22}{}^{c} = 0.0329$ [11]. Hydrogen diffusion at three temperatures (220, 250 and 280°C) were calculated by solving (23). **Figure** 4 is the equilibrium hydrogen distribution after 80 h of diffusion at 250°C. The shape of the hydrogen distribution is similar to that of hydrostatic stress. As expected, hydrogen atoms diffuse from a lower tensile hydrostatic region to a higher tensile hydrostatic region, and the peak content of hydrogen is reached at the position corresponding to the maximum tensile hydrostatic stress. **Figures** 5 **and** 6 are the peak content *vs.* time at the different loads and temperatures, respectively. It can be seen that the diffusion rate is fast in the first 10 h, but diffusion slows down in the later stage and reaches equilibrium at about 60 h. Figure 6 compares the peak values of equilibrium hydrogen content at the different temperatures. The peak value of hydrogen content decreases with the increase in temperature.

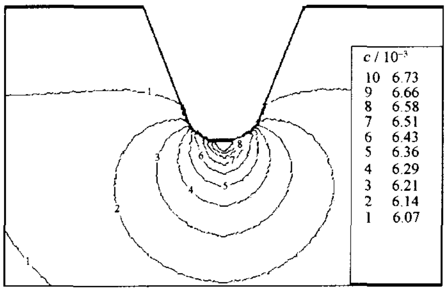

Figure 4 **Equilibrium** hydrogen **content distribution** *c* around the **notch** after 80 h of diffusion.

According to equation (22), the chemical potential of hydrogen is a function of both hydrogen composition and applied stress. Interstitial hydrogen atoms cause the lattice of the matrix to be distorted, thus increasing the chemical potential of the system. An applied tensile stress can ease the distortion of the lattice and thereby lower the chemical potential. Since the chemical potential of the system must reduce to the minimum in a spontaneous process, the diffusion process for hydrogen from the regions with lower tensile hydrostatic stresses to those with higher tensile hydrostatic stresses will continue until the chemical potential everywhere in the system reaches the same value.

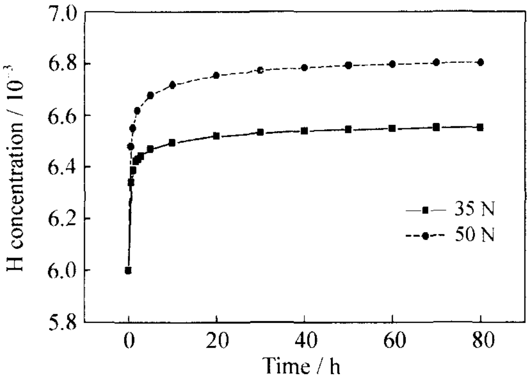

Figure 5 Hydrogen content as a function of time for two applied loads at 250°C.

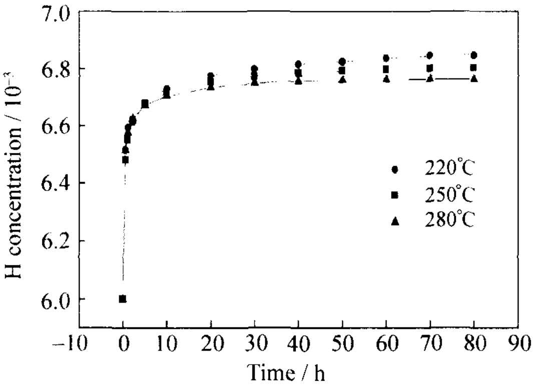

Figure 6 Hydrogen content as a function of time at different temperatures, the applied load is 50 N.

When the system reaches equilibrium, the equilibrium peak content of hydrogen may be roughly estimated as follows:

$$M\nabla\mu = M\nabla\mu_e + D\nabla c\left[1+\frac{c}{1-c}\right]=0 \qquad (25)$$

where $M=\frac{Dc}{RT}$, and μ_e includes the first five terms in equation (22). If μ_e is weakly dependent on the hydrogen content c, and if $c \ll 1$, then equation (25) can be solved as

$$c(\boldsymbol{r}) = c(\boldsymbol{r}_0)\mathrm{e}^{-\frac{\Delta\mu_e}{RT}} \qquad (26)$$

This is to say that, at equilibrium, the difference in c at two locations (r and r_0) is determined by their difference in μ_e. For a diluted solution of hydrogen, only the second term in μ_e is significant. Therefore, $\Delta\mu_e \approx -V_{\mathrm{mol}}C_{ijkl}\varepsilon_{kl}^{\mathrm{c}}\cdot\Delta\varepsilon_{ij}^{\mathrm{a}}$, which returns to the usual expression used by many literatures. By using equation (26), and assuming the plane strain condition, one can find the maximum equilibrium hydrogen content as $c_{\max}=1.14c_0$ at $T=250℃$, where c_0 is the far-field hydrogen content. This compares well with our simulation result of $c_{\max}= 1.13c_0$.

It is interesting to see how hydrogen redistribution might affect stress redistribution. The stress distribution induced by hydrogen interstitials is calculated as follows.

According to equation (11), the stress caused by the hydrogen diffusion is

$$\sigma_{ij}^{\mathrm{c}} = C_{ijkl}[\varepsilon_{ij}(\boldsymbol{r})-\varepsilon_{ij}^{\mathrm{c}}(\boldsymbol{r})] = C_{ijkl}\{\varepsilon_{ij}(\boldsymbol{r})-\varepsilon_{ij}^{\mathrm{c}}[c(\boldsymbol{r})-c_{\mathrm{m}}]\} \qquad (27)$$

where c_m is the average content of hydrogen.

From equation (15), in the Fourier space,

$$\varepsilon_{kl}(\boldsymbol{g}) = \frac{i}{2}[u_k(\boldsymbol{g})g_l + u_l(\boldsymbol{g})g_k] \qquad (28)$$

If we only consider the effect of hydrogen diffusion, then from equation (17),

$$u_k(\boldsymbol{g}) = -iG_{ik}(\boldsymbol{g})[\sigma_{ij}^{\mathrm{c}}\delta c(\boldsymbol{g})]\boldsymbol{g}_j \qquad (29)$$

$\varepsilon_{ij}(r)$ can be obtained from the inverse Fourier transformation of $\varepsilon_{ij}(g)$ and, therefore, the stress caused by hydrogen diffusion is calculated by equation (27).

Figure 7 shows the change in hydrostatic stress along the centerline of the notch induced by hydrogen redistribution after 80 h of diffusion. The maximum reduction in hydrostatic stress at the notch tip is about

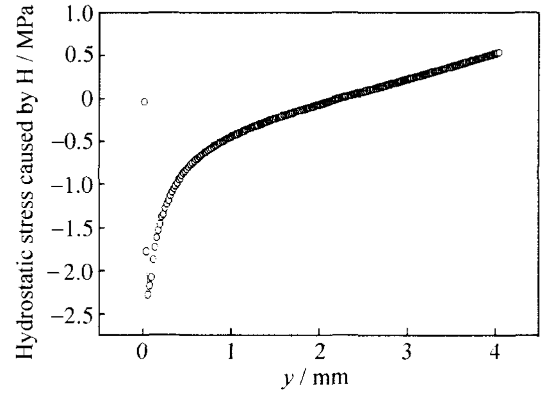

Figure 7 Change in hydrostatic stress along the centerline of the notch caused by interstitial hydrogen atoms after 80 h of hydrogen diffusion.

2.4 MPa, which is about 0.7% of the peak hydrostatic stress of 350 MPa. This indicates that, for a diluted solution, the stress redistribution due to the redistribution of hydrogen interstitial is insignificant.

4 Conclusion

The stress field of a cantilever zirconium specimen with a blunt notch was calculated by using the finite element method. Hydrogen diffusion under such a non-uniform stress field was then simulated by applying Khachaturyan's elastic theory and by solving the Cahn-Hilliard diffusion equation. The result shows that hydrogen atoms diffuse to the high-tensile hydrostatic region near the notch tip. The hydrogen content near the notch tip is increased by 13%, while the stress distribution around the notch is modified by hydrogen interstitials by only 0.7%. The diffusion process is faster in the first 10 h, during which the peak hydrogen content reaches 98% of its equilibrium value.

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