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VARIATION OF STRESSES AHEAD OF THE INTERNAL CRACKS IN $ReNi_5$ POWDERS DURING HYDROGEN CHARGING AND DISCHARGING CYCLES

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ABSTRACT

In this study, the evolution of the stress-states ahead of the penny shaped internal cracks in both spherical and disk shaped $ReNi_5$ particles during hydrogen charging and discharging cycles were investigated using coupled diffusion/deformation FEM analyses. The results indicate that large tensile stresses, on the order of 20-30% of the modulus of elasticity, develop in the particles. The disk shaped particles, in addition to having faster charging/discharging cycles, may offer better resistance to fracture than the spherical particles.

INTRODUCTION

The application of hydride-forming $ReNi_5$ compounds, where Re denotes the rare earths La, Ce, and Misch-metals, in re-chargeable nickel metal hyride batteries is well known[1-4]. In the case of $LaNi_5$, a large amount of hydrogen can be absorbed to form $LaNi_5H_{6.7}$ at nearly room temperature[1]. The calculated density of the absorbed hydrogen is about a factor of two higher than the density of liquid hydrogen[5]. The lattice dimensions of unsaturated $LaNi_5$ are about a=5.017A° and c=3.982A°, and after saturation with hydrogen, the lattice parameters increase to about a=5.440A° and c=4.310A° which represents a volume expansion of over 25% [3]. Associated with this large volume expansion, the hydrogenation cycles produce very fine powders through a cleavage fracture of initial particles leading to reductions in battery performance.

In this study, to elucidate the stress-states in the particles during the hydrogen charging and discharging cycles a set of coupled diffusion/deformation finite element analyses are performed. The role of the particle shape on the evolution of the stress-states ahead of the penny shaped internal cracks is investigated.

DETAILS OF THE FEM ANALYSES

The hydrogen diffusion into $ReNi_5$ is assumed to be a bulk diffusion process driven by chemical potential [5]which can be described by the general behavior:

$$J = -sD\left[\kappa_s \frac{\partial}{\partial x}(\ln\tilde{\theta}) + \frac{\partial\phi}{\partial x}\right] \quad (1)$$

where J is the flux concentration of the diffusing phase, $D(c,\tilde{\theta})$ is the diffusivity, $s(\tilde{\theta})$ is the solubility, $\kappa_s(c,\tilde{\theta})$ is the "Soret effect" factor providing diffusion because of a possible temperature gradient, $\tilde{\theta}$ is the absolute temperature, and ϕ is the normalized concentration (often also referred to as the "activity" of the diffusing material), $\phi = c/s$ in which c is the mass concentration of the diffusing material in the base material. During the hydrogen charging and discharging cycles, the stress-strain behavior of the powders is assumed to be elastic:

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$$\sigma = \mathbf{D}\left(\varepsilon_D + \varepsilon_V(\phi)\right) \qquad (2)$$

where $\mathbf{D}$ is the elasticity matrix, ε_D is the deviatoric component of the total strain and $\varepsilon_V(\phi)$ is the volumetric strain which is a function of the normalized hydrogen concentration. During the analyses, it was assumed that both the diffusion parameters and the elastic properties remain constant in spite of possible phase changes; also, temperature effects were neglected. Throughout the study, the time values were normalized with the coefficient of the diffusion, all the stress values were normalized with the value of the Young's modulus and the concentration values were normalized with the solubility value, thus yielding results that are independent of the material parameters.

RESULTS

In the next set of simulations the charging and discharging behavior of a spherical particle containing a penny shaped internal crack were studied. To model the crack tip singularity, collapsed elements having shifted mid-side nodes[6] were used at immediate crack tip region in these analyses. Penetration of the crack faces resulting from the volume expansion was prevented by using a series of non-dimensional interface elements[7] along the crack surfaces. No hydrogen was present in the particles at the beginning of the solution. The evolution of the stress state in the particle during the hydrogen charging cycle is summarized in Fig. 1 (left). In this figure, the crack tip is located at $x/r = 0.4$; x/r values smaller than this value represent the crack wake region and larger values are for the regions ahead of the crack tip. Because of the embedded nature of the crack, the development of the hydrogen concentration profiles was identical to that seen for a spherical particle without an internal crack. As can be seen from the figure, large normal stress values develop ahead of the crack tip even at very early stages of the charging. This increase continuous and reaches a value as high as half of the modulus of elasticity. The attainment of this peak value occurred shortly before reaching a fully charged stage, then a slight reduction took place. Nevertheless, the stress level remained significantly high at the fully charged stage. Fig. 1 (right) shows the stress-states in the same particle during the discharging cycle, respectively. The zero value of the normalized time corresponds the fully charged state in the figure. With the loss of the hydrogen in the regions near to the particle surface, a stress redistribution takes place and the crack tip stresses relax significantly at very early stages of the discharging cycle. As can be seen from the figure, the stress distribution at the interior regions of the particle becomes quite uniform, as if there is no crack, resulting from the closure of the crack faces due to overall contraction.

In next set of simulations the behavior of disk shaped particles containing a penny shaped internal crack was investigated. The volume of this disk shaped particle and also the size of the penny shaped crack were identical to that of spherical particle. The development of the stress-states in the disk shaped particle containing the penny shaped crack during the hydrogen charging cycle is shown in Fig. 2 (right). The normalized time of 0.0518 corresponds to fully charged state in the figure. When a comparison is made with the previous spherical particle case, a significant reduction in the charging time can be observed. This reduction arises from the larger surface-area/volume ratio of the disk shaped particle. As can be seen from the figure, in spite of the presence of an internal crack, the stress distribution at fully charged state was very uniform which is opposite to that seen for the spherical particle containing a penny shaped crack (Fig.1). The shape changes of this disk shaped particle during the same time intervals given in

Fig. 2 (right) are shown in Fig. 3. As can be seen from the figure, resulting from the fast diffusion of the hydrogen from both top and side surfaces, a large expansion occurs near the corner regions. This expansion introduces a compression in the central regions leading to the stress distribution seen in Fig. 2 (right). This can also be substantiated from the crack opening behavior during the charging cycle as seen in Fig. 4. Shortly after this opening, the crack tip region closes again due to the evolution of the compression in the central regions of the particle as described earlier. The variations in the stress values during the discharging cycle of the same particle with the internal crack are summarized in Fig. 2 (left). As can be seen from the figure, no stress elevation also takes place during the discharging cycle associated with the aforementioned shape changes.

CONCLUSIONS

In this study, the development of the stress-states in $ReNi_5$ particles during hydrogen charging and discharging cycles was investigated by using coupled diffusion/deformation FEM analyses. The results indicate that:

1. Large tensile stresses, on the order of 20-30% of the modulus of elasticity, develop in the particles.
2. The disk shaped particles, in addition to having faster charging/discharging cycles, may offer better resistance to fracture than the spherical particles

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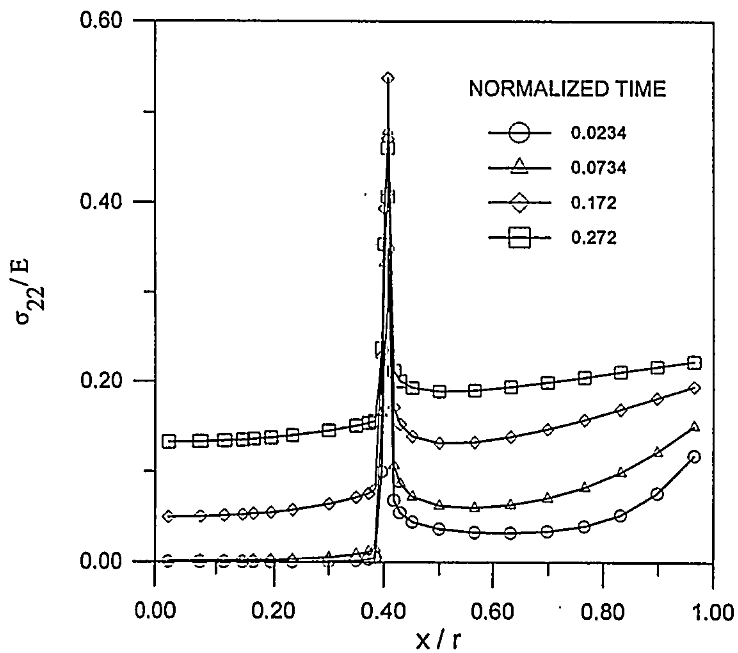


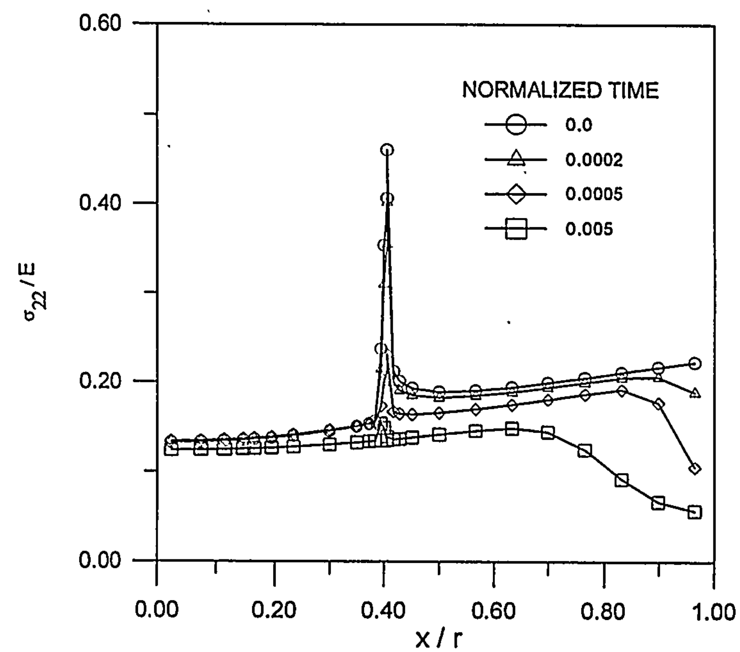
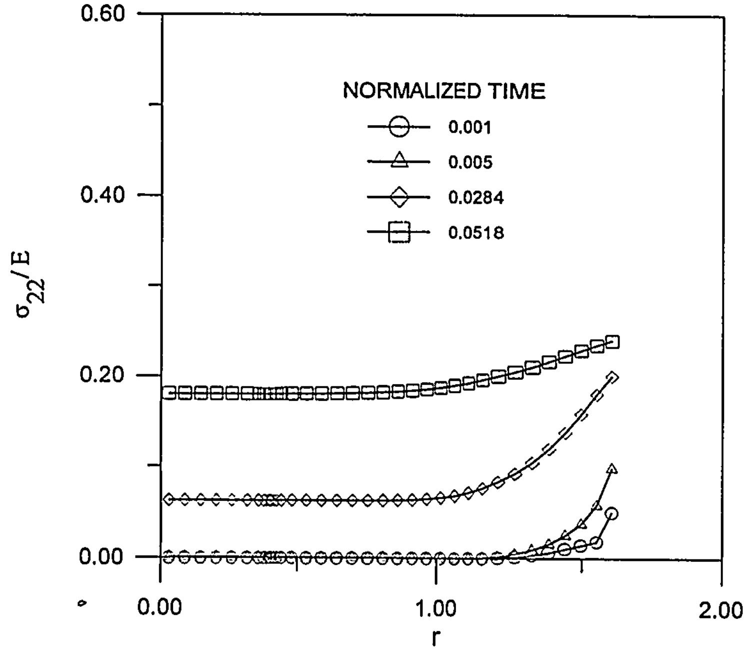


Fig.1 Evolution of the tensile stress ahead of the penny shaped crack in a shperical partical during hydrogen charging (left) and discharging (right) cycles.



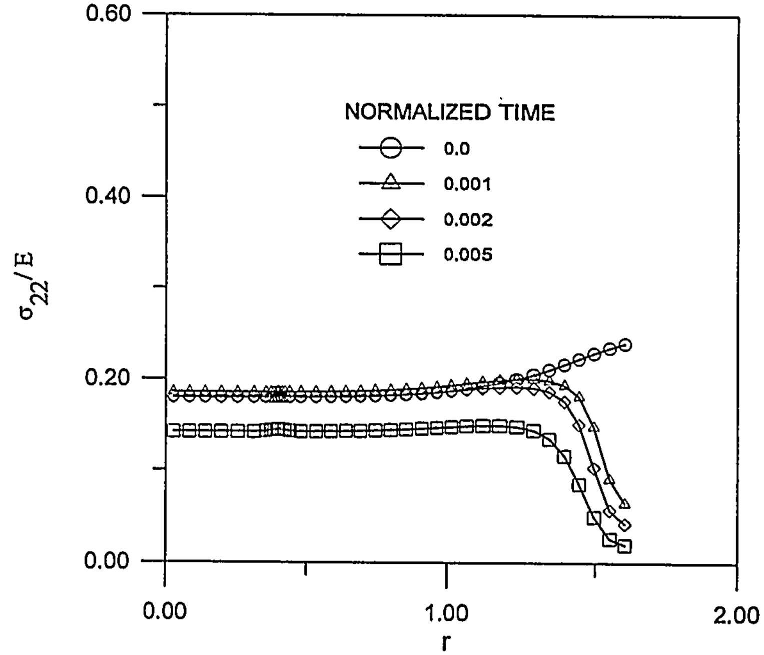


Fig.2 Evolution of the tensile stress ahead of the penny shaped crack in a disk shaped partical during hydrogen charging (left) and discharging (right) cycles.

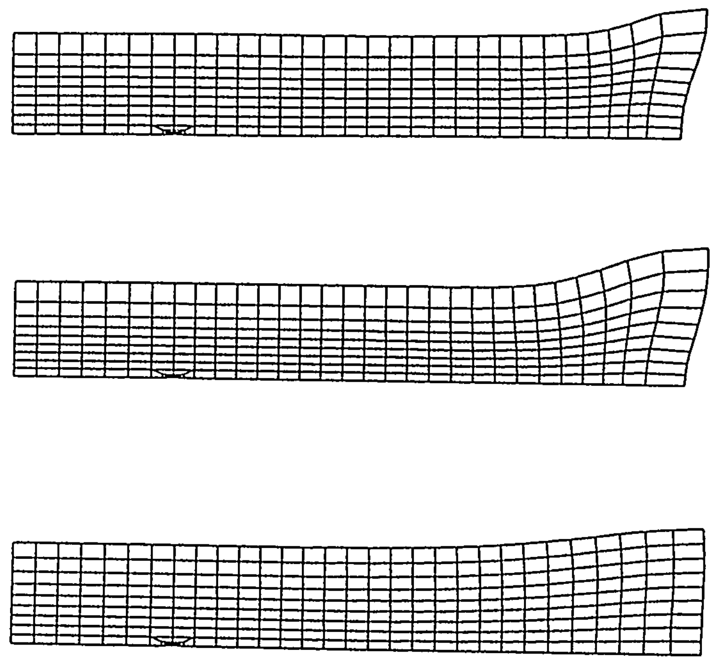


Fig.3 The shape changes in the disk shaped particle with a penny shaped crack during hydrogen charging cycle. The normalized times are: top, 0.001, middle, 0.0284 and bottom, 0.0518.

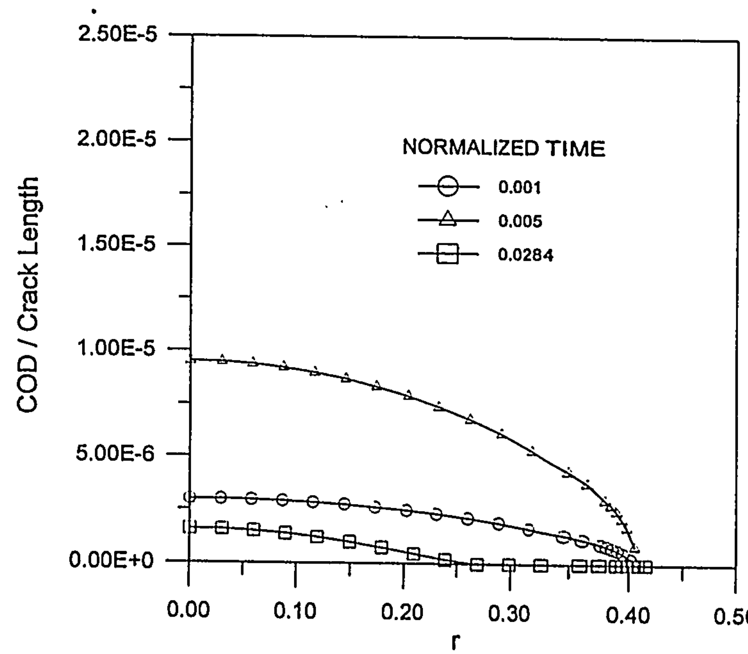


Fig.4 Crack opening profiles of the penny shaped internal crack in the disk shaped particle during hydrogen charging cycle.