MODELING HYDROGEN TRANSPORT THROUGH TUBULAR MEMBRANES

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Abstract. *In this paper we present a continuum model, along with its numerical implementation, for hydrogen transport through tubular membranes. This work is a streamlined version of the one presented by the authors in Duda et al., 2006, in which a fully coupled three-dimensional continuum model for deformation, degradation and solute diffusion was developed. The continuum model is described within the framework of modern continuum mechanics whereas the corresponding numerical implementation is based on the finite element method and an Euler implicit scheme for spatial and temporal discretizations, respectively. An illustrative example related to the hydrogen transport through tubular membranes of Palladium coated Niobium is presented. Degradation is not accounted for in this paper.*

Keywords: *Multifield continuum mechanics, solute diffusion, hydrogen embrittlement*

1. INTRODUCTION

The subject of hydrogen transport in solids has been studied extensively for decades due to its scientific and technological relevance (see, for instance, Sofronis, 1995; Zoltowski, 1999; Buxbaum and Kinney, 1996; Wang *et al.*, 2002). In fact, hydrogen transport in metals plays a dominant role in environmentally assisted degradation as well as in pure hydrogen production. In the latter case, palladium membranes have been used for hydrogen extraction for semiconductor manufacture, fuel cells, and laboratory use, mainly because of palladium superior quality in terms of permeability, surface properties, hydrogen transport selectivity and resistance to high temperatures, corrosion and solvents. In addition, palladium is easily formed into tubes that are easily fabricated into hydrogen extraction units. These features make palladium membranes very attractive for use with petrochemical gases. Despite its advantages, palladium is very expensive and soft, which has led to development of palladium composite membranes,e.g., the tubular membranes of palladium-coated niobium and tantalum discussed in Buxbaum and Kinney, 1996.

Motivated by the above considerations, we present in this paper a streamlined version of the continuum model developed by authors in Duda *et al.*, 2006, along with its numerical implementation, aiming at the modeling of hydrogen transport through tubular palladium membranes. The governing equations of the theory, which is developed within the framework of continuum mechanics, are obtained by combining the basic balances with a constitutive theory compatible with the dissipation inequality. They account for the deformation-diffusion coupling by means of the hydrogen induced strain and stress assisted diffusion. The numerical model is constructed by using the finite element method, the backward implicit Euler method and a staggered scheme to solve the discrete system of coupled equations.

2. THE CONTINUUM MODEL

In this section we briefly present the coupled model for deformation and solute diffusion in solids.

2.1 Basic Laws

We consider a continuum body $\mathcal{B}$, identified with the region of space it occupies in a fixed reference configuration, kinematically described by the macroscopic motion $\mathbf{y}$; the solute concentration c and the solute flux $\mathbf{J}$, a rate type variable representing the local motion of the solute relative to the motion of the underlying solid. We consider the Principle of Virtual Power, the solute mass balance and the dissipation inequality as the basic laws of the theory. By the Principle of Virtual Power, four balanced force systems are introduced, one for each kinematical descriptor: i) the standard or macroscopic force system, which is described by the macro stress $\mathbf{S}$ and the external body force $\mathbf{b}$, ii) the microforce system associated with the solute concentration c, which is described by the micro stress Γ, the external and internal microforce γ^e and γ^i, respectively, iii) the microforce system associated with the solute flow $\mathbf{J}$, which is characterized by the micro stress Σ, the external and internal microforce Υ^e and Υ^i, respectively. The aforementioned force balances localize into:

$$\text{Div}\mathbf{S} + \mathbf{b} = \mathbf{0},$$

$$\text{Div}\Gamma - \gamma^i + \gamma^e = 0, \tag{1}$$

$$\text{Div}\Sigma - \Upsilon^i + \Upsilon^e = \mathbf{0}.$$

The solute mass balance localizes into:

$$\dot{c} = -\text{Div}\mathbf{J} + h, \tag{2}$$

where h is the solute supply rate.

Within the present context, the local version of the dissipation inequality is written as:

$$\dot{\psi} \leq \mathbf{S} \cdot \dot{\mathbf{F}} + \Gamma \cdot \nabla\dot{c} + (\gamma^i + \mu)\,\dot{c} + (\Sigma + \mu I) \cdot \nabla\mathbf{J} + \Upsilon^i \cdot \mathbf{J}, \tag{3}$$

where ψ is the free energy density, μ is the chemical potential and $\mathbf{F} := \nabla\mathbf{y}$ is the deformation gradient.

2.2 Constitutive Theory

Following the dissipation inequality (3), we consider constitutive equations for the quantities:

$$\psi = \hat{\psi}(\mathsf{p}), \quad \mathbf{S} = \hat{\mathbf{S}}(\mathsf{p}), \quad \Gamma = \hat{\Gamma}(\mathsf{p}), \quad \gamma := \gamma^i + \mu = \hat{\gamma}(\mathsf{p}), \quad \Sigma + \mu I = \hat{\Sigma}(\mathsf{p}), \quad \Upsilon^i = \hat{\Upsilon}(\mathsf{p}), \tag{4}$$

with $\mathsf{p} := (\mathsf{e}, \mathbf{J})$, where $\mathsf{e} := (\mathbf{F}, c, \nabla c)$. Restrictions provided by the Dissipation Principle can be obtained via the Coleman-Noll procedure (see Silhavy, 1997). It can be shown that the aforementioned restrictions are the following:

i) Equilibrium relations:

$$\psi(\mathsf{p}) = \psi(\mathsf{e}), \quad \hat{\mathbf{S}} = \frac{\partial\hat{\psi}}{\partial\mathbf{F}}, \quad \hat{\Gamma} = \frac{\partial\hat{\psi}}{\partial\nabla c}, \quad \hat{\gamma} = \frac{\partial\hat{\psi}}{\partial c}, \quad \hat{\Sigma} = 0; \tag{5}$$

ii) Reduced dissipation inequality:

$$\hat{\Upsilon}(\mathsf{p}) \cdot \mathbf{J} \geq 0. \tag{6}$$

Therefore, the theory is constitutively specified by choosing the response functions $\hat{\psi}$ and $\hat{\Upsilon}$, the latter consistent with the inequality (6). It can be shown that, under mild smoothness assumptions, the most general representation for $\hat{\Upsilon}$ is as follows:

$$\hat{\Upsilon}(\mathsf{p}) = \hat{\mathbf{H}}(\mathsf{p})\mathbf{J}, \tag{7}$$

In addition, we assume that $\hat{\mathbf{H}}$ do not depend on $\mathbf{J}$. Therefore, the reduced dissipation inequality is satisfied if and only if $\hat{\mathbf{H}}$ is positive semi-definite.

3. SPECIAL THEORY

The formal procedure to obtain a small strain version of the present theory involves linearization. In that case it is enough to replace the deformation gradient $\mathbf{F}$ by the small strain tensor:

$$\mathbf{E} := \frac{1}{2}\left(\nabla\mathbf{u} + \nabla\mathbf{u}^\top\right) =: \nabla\mathbf{u}^S \tag{8}$$

in all equations of the previous subsection, as well as to consider $\hat{\psi}$ quadratic on $\mathbf{E}$. Also, the theory is limited to the isotropic case and all the couplings are implemented via the free energy response $\hat{\psi}$. From now on we assume that $\gamma^e = h = 0$ and $\Upsilon^e = \mathbf{0}$. The others constitutive choices are:

i) Free energy response:

It is assumed the following additive decomposition for the free energy response:

$$\hat{\psi}(\mathbf{E}, c) = \hat{\varepsilon}(\mathbf{E}, c) + \alpha(\ln c - 1)c, \tag{9}$$

where the parameter α is given by: $\alpha = \dfrac{kT}{v}$, where k is Boltzmann's constant, T is the absolute temperature, and v is the lattice volume per host lattice atom. The strain energy response $\hat{\varepsilon}$ is:

$$\hat{\varepsilon}(\mathbf{E}, c) = \bar{\lambda}(\text{tr } \mathbf{E}_e)^2 + 2\bar{\mu}|\mathbf{E}_e|^2, \quad \text{where} \quad \mathbf{E} = \mathbf{E}_e + e(c - c_0)\mathbf{I} \tag{10}$$

is the additive decomposition of the strain into its elastic and chemical parts. In the strain energy, $\bar{\lambda}$ and $\bar{\mu}$ are Lame parameters. In the chemical part of the strain, e denotes strain brought about by a solute concentration change of one atom per host lattice atom, in the absence of any stress, and c_0 is a solute reference concentration. We consider the solute concentration measured in hydrogen atoms per host lattice atom;

ii) Dissipative response:

$$\hat{\mathbf{H}}(\mathsf{p}) = \frac{D}{\alpha\, c}\mathbf{I}, \tag{11}$$

where D is the diffusion coefficient.

With the above assumptions, the linear elasticity coupled with diffusion problem can be stated as follows:

Problem:

Given: Boundary/initial conditions, material and geometrical parameters, body force density and reference concentration,

Find: The displacement $\mathbf{u}$ and the concentration c satisfying the following equations:

$$\text{Div}\mathbf{S} + \mathbf{b} = \mathbf{0},$$
$$\mathbf{S} = \bar{\lambda}\,(\text{tr}\mathbf{E})\mathbf{I} + 2\bar{\mu}\mathbf{E} - e(3\bar{\lambda} + 2\bar{\mu})(c - c_o)\mathbf{I}, \quad \mathbf{E} = \nabla\mathbf{u}^S,$$
$$\text{Div}\mathbf{J} + \dot{c} = 0, \tag{12}$$
$$\mathbf{J} = -D\left(\nabla c - \frac{e}{\alpha}\, c\, \nabla(\text{tr}\mathbf{S})\right).$$

4. WEAK FORMS

The governing equations (12) in their weak forms, are:

Given: Boundary/initial conditions, material and geometrical parameters, body force density and reference concentration,

Find: $\mathbf{u}$ and c satisfying the following equations:

$$\int_{\mathcal{B}} (\mathbf{S} \cdot \nabla\mathbf{v} - \mathbf{b} \cdot \mathbf{v})\, dV = 0 \quad \forall\, \mathbf{v} \in \mathbf{V}^0,$$
$$\int_{\mathcal{B}} (\mathbf{J} \cdot \nabla\varphi - \dot{c}\,\varphi)\, dV = 0 \quad \forall\, \varphi \in V^0, \tag{13}$$

where:

V^0 and $\mathbf{V}^0$ are appropriate functional spaces,

$$\mathbf{S} = \bar{\lambda}\,(\text{tr}\mathbf{E})\mathbf{I} + 2\bar{\mu}\mathbf{E} - e(3\bar{\lambda} + 2\bar{\mu})(c - c_o)\mathbf{I}, \quad \mathbf{E} = \nabla\mathbf{u}^S, \tag{14}$$
$$\mathbf{J} = -D\left(\nabla c - \frac{e}{\alpha}\, c\, \nabla(\text{tr}\mathbf{S})\right).$$

The solution and test spaces (functional spaces) are approximated by finite dimensional spaces by using the finite element method. The approximated fields are denoted by $\mathbf{u}_h$, c_h, $\mathbf{v}_h$ and φ_h. Besides Euler implicit scheme is adopted to the temporal discretization, i.e., the problem is reduced to the solution of the set of equations for each time instant t_k, where: $\dot{f}^k \approx \dfrac{f^k - f^{k-1}}{t_k - t_{k-1}}$, $f^k := f(t_k)$. With these definitions, the weak forms (13) are written as:

$$\int_{\mathcal{B}} \left(\mathbf{S}_h^k \cdot \nabla\mathbf{v}_h - \mathbf{b} \cdot \mathbf{v}_h\right)\, dV = 0,$$
$$\int_{\mathcal{B}} \left(\mathbf{J}_h^k \cdot \nabla\varphi_h - \dot{c}_h^k\,\varphi_h\right)\, dV = 0, \tag{15}$$

for all $\mathbf{v}_h$ and φ_h, with $\mathbf{S}_h^k$ and $\mathbf{J}_h^k$ having obvious definitions.

5. NUMERICAL RESULTS

In this section solutions to the initial boundary value problem of transient hydrogen diffusion coupled with material elasticity are presented. As described in Buxbaum and Kinney, 1996, we consider hydrogen transport through tubular membranes of Palladium and Niobium, at room temperature, in the following two problems:

1. A Palladium membrane 10.0 mm in internal diameter and 0.07 mm in thickness;

2. A 10^{-3} mm Palladium coated niobium membrane 10.0 mm in internal diameter and 0.07 mm in thickness.

The material properties are shown in Table 1 (see Sofronis, 1995).

Table 1: Material properties for the metals with internal hydrogen

Parameters	Palladium (Pd)	Niobium (Nb)
$\bar{\lambda}$	132.0 GPa	150.3 GPa
$\bar{\mu}$	44.0 GPa	30.78 GPa
D	$1.0\text{x}10^{-8}$ m²/s	$1.0\text{x}10^{-8}$ m²/s
α	$6.18\text{x}10^{8}$ J/m³	$5.31\text{x}10^{8}$ J/m³
e	0.0633	0.0576

The boundary conditions used are: the solute concentration, measured in hydrogen atoms (H) per host lattice atom (Pd), on the internal and external surface: $c_i = 2.44\text{x}10^{-3}$ H/Pd, $c_e = 1.74\text{x}10^{-3}$ H/Pd. The pressure on the internal and external surface: $p_i = \mathbf{S}\mathbf{n}_i = 6.9\text{x}10^{-5}$ GPa, $p_e = \mathbf{S}\mathbf{n}_e = 3.5\text{x}10^{-5}$ GPa, where $\mathbf{S}$ is the stress tensor and $\mathbf{n}_{i,e}$ are the normal vectors on the internal and external surface, respectively. These conditions were adopted in order to mimic the situation described in Buxbaum and Kinney, 1996, in which atomic hydrogen migrates from the internal surface towards the external surface during a purification process.

A transient analysis concerning the tubular membranes was performed and some of the results are depicted in Figures 1, 2 and 3, at different times. The figures 1 (a) and (b) represent the radial distribution of solute concentration of Palladium membrane, and Palladium coated niobium membrane, respectively. We can observe the effect of the material change on the external and internal surfaces of the tube. Figures 2 (a) and (b) represent the radial distribution of hydrostatic stress of Palladium membrane, and Palladium-coated niobium membrane, respectively. Again, it is important to observe the effect of the material change. Figures 3 are equivalent to figures 2, but are displayed only at the central portion of the tube, in order to amplify the curves.

(a) Palladium membrane
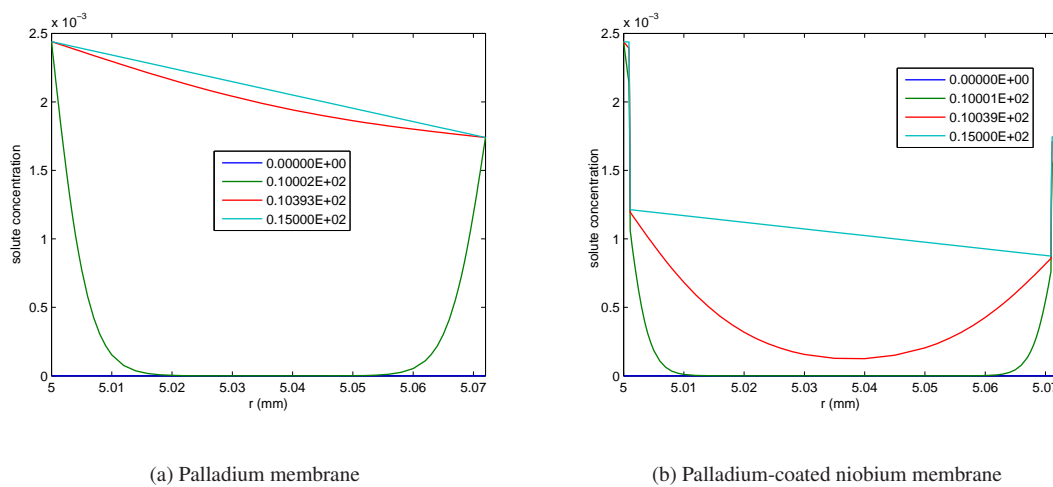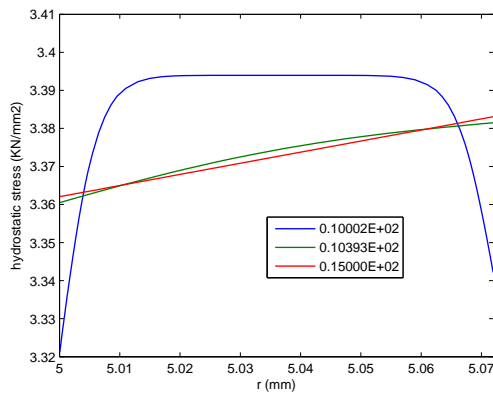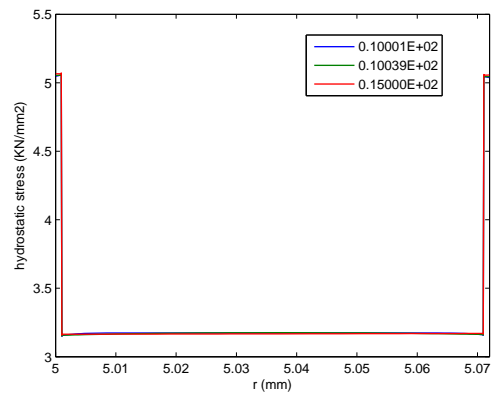
(b) Palladium-coated niobium membrane

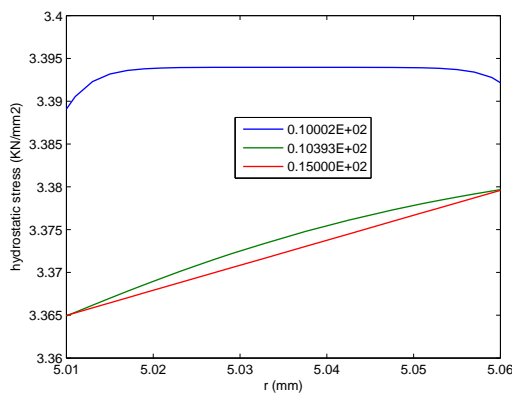Figure 1. Solute concentration distribution at different times.
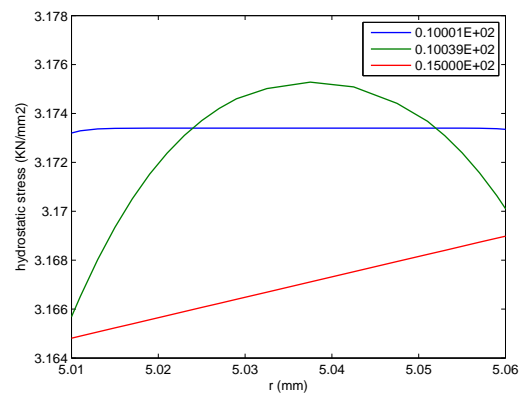
(a) Palladium membrane

(b) Palladium-coated niobium membrane

Figure 2. Hydrostatic stress distribution at different times.

(a) Palladium membrane

(b) Palladium-coated niobium membrane

Figure 3. Hydrostatic stress distribution at the central portion at different times.

6. CONCLUSIONS

This paper presents preliminary results concerning the hydrogen transport through tubular membranes of Palladium coated Niobium. To obtain these results we have used the coupled model developed by the authors in Duda *et al.*, 2006, for deformation, degradation and solute diffusion in elastic solids, although the degradation had not been considered. The formulation was carried out within the framework of continuum mechanics, in which additional kinematical fields were introduced in order to describe damage and diffusion processes. The governing equations were obtained by combining the basic balances with a constitutive theory compatible with the dissipation inequality. The numerical implementation was based on the finite element method, the backward implicit Euler method and a staggered scheme to solve the resulting discrete coupled system of equations. The illustrative example presented addressed the capability of the proposed numerical model to account for the deformation-diffusion coupling. The preliminary results so obtained were very satisfactory.

7. ACKNOWLEDGEMENTS

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