A thermo-mechanically-coupled theory accounting for hydrogen diffusion and large elastic–viscoplastic deformations of metals

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ABSTRACT

In this paper we develop a thermodynamically-consistent coupled-theory which accounts for diffusion of hydrogen, diffusion of heat, and large elastic–viscoplastic deformations of metals. The theory should be of utility in the analysis of hydrogen diffusion in elastic–plastically-deforming solids, an analysis which is an essential prerequisite for theoretical and numerical efforts aimed at modeling the integrity of structural components used for hydrogen gas storage and distribution.

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1. Introduction

Since the combustion of hydrogen produces only water as the combustion product, hydrogen is expected to play an increasingly important role as a "clean" fuel in the future.[1] However, hydrogen is a gas at ambient conditions, and the storage and distribution of hydrogen in its molecular or atomic form is a materials challenge (cf., e.g., Züttel et al., 2010). Atomic hydrogen, being the smallest of gaseous impurities, readily dissolves in and permeates through most materials. Hydrogen dissolution and permeation can be significant at high pressures which are expected to approach 100 MPa in some cases, and since hydrogen can embrittle materials it may affect the integrity of structural components used for hydrogen storage and distribution. Accordingly, it is important to understand and model the *coupled* diffusion-mechanics response of metallic components used to contain this gas, and this topic is receiving increasing attention because of its potential application to the development of the emerging technology of large-scale production, storage and distribution of hydrogen (cf., e.g., San Marchi et al., 2007; Dadfarnia et al., 2009, 2010).

The deleterious effects of hydrogen on the mechanical response of iron and steel are well-known (cf., e.g., Hirth, 1980). The precise microscopic mechanisms by which hydrogen embrittles steels are still not very well understood or modeled. This topic continues to be the focus of intensive theoretical and experimental research (cf., e.g., Serebrinsky et al., 2004; Ramasubramaniam et al., 2008; Novak et al., 2010; Dadfarnia et al., 2010),[2] and is *not the focus of this paper*. Instead, our focus here is on the development of a continuum-level theory for the diffusion of hydrogen, coupled with the thermo-elastic–plastic response of materials, which, as emphasized by Birnbaum and Sofronis (1994), is an essential prerequisite to any attempt to address the issue of hydrogen-embrittlement-related failures in structural components.

It has long been observed that there is an asymmetry between the kinetics of absorption and the kinetics of evolution of hydrogen in steels, in that absorption proceeds with a larger apparent diffusivity than does evolution. This asymmetry in diffusivities is attributed to trapping of the hydrogen atoms at various microstructural "trapping sites," which include interfaces between the matrix and various second-phase particles, grain boundaries, and dislocation cores. A widely-used micro-mechanical model for describing this asymmetry in diffusivities, is that of Oriani (1970). His model is

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[1] Hydrogen is produced from water by electricity through an electrolyser, and the hydrogen so-produced is a "renewable" fuel only if it is produced directly from solar light, or indirectly from a renewable source, e.g., wind- or hydro-power (Züttel et al., 2010).

[2] As reviewed by Dadfarnia et al. (2010), research to date has identified the following two major mechanisms for hydrogen embrittlement: (i) hydrogen-enhanced decohesion—a mechanism induced by the segregation of hydrogen to microstructural interfaces such as grain-boundaries and particle/matrix interfaces, which leads to a reduction in the cohesive strength of the material; and (ii) hydrogen-enhanced localized plasticity—a mechanism induced by the segregation of hydrogen to dislocation cores, which leads to a reduction of the strength of barriers to dislocation motion, and thereby a reduction in the resistance to plastic flow.

based on a crucial assumption regarding the effects of the microstructure on hydrogen transport and trapping. Oriani postulated that within a continuum-level material point, the microstructure affects the local distribution of hydrogen in a manner such that population of hydrogen in trapping sites is always in *equilibrium* with the population associated with normal lattice sites.

There is a long history of the study of species diffusion coupled to elasticity, and the status of mathematical modeling of the coupled diffusion–deformation interactions of interstitial (as well as substitutional) solutes in crystalline solids undergoing small elastic deformations, has been reviewed, in a classical paper, by Larché and Cahn (1985). One of the earliest papers which attempts to couple nonlinear diffusion of hydrogen with large *elastoplastic* deformation of metals is the seminal paper of Sofronis and McMeeking (1989), who formulated a theory which has Oriani's postulate of "local equilibrium" as one of its central ingredients. The theory of Sofronis and McMeeking was extended by Krom et al. (1999) to account for the effects of an increase in the number of trapping sites due to plastic deformation. This latter form of the theory, with minor modifications, is the one which is at present most often used to analyze the effects of interactions of hydrogen transport, elastic–plastic deformation, lattice-dilatation, and hydrogen-induced reduction of the resistance to plastic flow. A summary of this currently used coupled-theory may be found in Dadfarnia et al. (2009) and Miresmaelili et al. (2010), and references to the literature therein.

The purpose of this paper is to develop a thermo-mechanically-coupled theory accounting for hydrogen transport and large elastic–viscoplastic deformations within a modern continuum-mechanical framework. In doing so, we find that we cannot readily incorporate microstructural-level considerations of lattice and trapping sites and distinctions between lattice diffusivities and effective diffusivities. Although the experimental evidence of hydrogen-trapping is incontrovertible, we find Oriani's microstructural hypothesis to be of dubious validity and limited usefulness in formulating a *consistent continuum-level coupled theory*. Accordingly, in our continuum theory we do not attempt to explicitly incorporate microstructural considerations of lattice sites and trapping sites, and the attendant hypothesis of Oriani. Therefore the hydrogen diffusivity that we shall consider in our theory will de facto be an *effective continuum-level diffusivity*.

In formulating our theory, we limit our considerations to isotropic materials at low homologous temperatures,[3] and for these conditions we develop a reasonably general theory in Sections 2–8. We summarize the general theory in Section 9. In Section 10 we discuss a special set of constitutive equations which should be useful for applications. The specialized theory is similar in spirit to the theory of Sofronis–McMeeking, but has the following distinctive characteristics: (i) it is phrased entirely at the continuum-level; (ii) it is consistent with modern continuum thermodynamics; (iii) it is properly frame-indifferent; (iv) it uses modern $\mathbf{F} = \mathbf{F}^e\mathbf{F}^p$ kinematics to describe large elastic–plastic deformations; (v) it allows for thermally-activated rate-dependent plastic flow; and (vi) it is not restricted to isothermal conditions.

We emphasize that the purpose of this paper is only to report on the formulation of the theory. We leave a report concerning its numerical implementation and use for analysis of hydrogen transport, and the more difficult problem of hydrogen embrittlement, to future work.

2. Kinematics

Consider a macroscopically-homogeneous body B with the region of space it occupies in a fixed *reference configuration*, and de-

note by $\mathbf{X}$ an arbitrary material point of B. A *motion* of B is then a smooth one-to-one mapping $\mathbf{x} = \boldsymbol{\chi}(\mathbf{X}, t)$ with *deformation gradient*, *velocity*, and *velocity gradient* given by[4]

$$\mathbf{F} = \nabla\boldsymbol{\chi}, \quad \mathbf{v} = \dot{\boldsymbol{\chi}}, \quad \mathbf{L} = \operatorname{grad} \mathbf{v} = \dot{\mathbf{F}}\mathbf{F}^{-1}. \tag{2.1}$$

Following modern developments of large-deformation plasticity theory (cf., e.g., Anand and Gurtin, 2003; Gurtin and Anand, 2005), we base our theory on the Kröner (1960) decomposition

$$\mathbf{F} = \mathbf{F}^e\mathbf{F}^p, \tag{2.2}$$

of the deformation gradient. Here, suppressing the argument t:

(i) $\mathbf{F}^e(\mathbf{X})$ represents the local deformation of material in an infinitesimal neighborhood of $\mathbf{X}$ due to stretch and rotation of the microscopic lattice structure; and

(ii) $\mathbf{F}^p(\mathbf{X})$ represents the local deformation in an infinitesimal neighborhood of material at $\mathbf{X}$ due to the motion of dislocations.

We refer to $\mathbf{F}^e$ and $\mathbf{F}^p$ as the *elastic and plastic distortions*, and we refer to the local space at $\mathbf{X}$ represented by the range of $\mathbf{F}^p(\mathbf{X})$, as a local *structural space*.[5]

We assume that

$$J \stackrel{\text{def}}{=} \det \mathbf{F} > 0 \tag{2.3}$$

and hence, using (2.2),

$$J = J^e J^p, \quad \text{where} \quad J^e \stackrel{\text{def}}{=} \det \mathbf{F}^e > 0 \quad \text{and} \quad J^p \stackrel{\text{def}}{=} \det \mathbf{F}^p > 0, \tag{2.4}$$

so that $\mathbf{F}^e$ and $\mathbf{F}^p$ are invertible.

The right polar decomposition of $\mathbf{F}^e$ is given by

$$\mathbf{F}^e = \mathbf{R}^e\mathbf{U}^e, \tag{2.5}$$

where $\mathbf{R}^e$ is a rotation, while $\mathbf{U}^e$ is a symmetric, positive-definite tensor with

$$\mathbf{U}^e = \sqrt{\mathbf{F}^{e\top}\mathbf{F}^e}. \tag{2.6}$$

As is standard, we define

$$\mathbf{C}^e = \mathbf{U}^{e2} = \mathbf{F}^{e\top}\mathbf{F}^e, \tag{2.7}$$

and refer to

$$\mathbf{E}^e = \frac{1}{2}(\mathbf{C}^e - \mathbf{1}), \tag{2.8}$$

as the *elastic strain*.

By (2.1)$_3$ and (2.2),

$$\mathbf{L} = \mathbf{L}^e + \mathbf{F}^e\mathbf{L}^p\mathbf{F}^{e-1}, \tag{2.9}$$

with

$$\mathbf{L}^e = \dot{\mathbf{F}}^e\mathbf{F}^{e-1}, \quad \mathbf{L}^p = \dot{\mathbf{F}}^p\mathbf{F}^{p-1}. \tag{2.10}$$

The elastic and inelastic stretching and spin tensors are defined through

$$\left.\begin{array}{ll} \mathbf{D}^e = \operatorname{sym} \mathbf{L}^e, & \mathbf{W}^e = \operatorname{skw} \mathbf{L}^e, \\ \mathbf{D}^p = \operatorname{sym} \mathbf{L}^p, & \mathbf{W}^p = \operatorname{skw} \mathbf{L}^p, \end{array}\right\} \tag{2.11}$$

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[3] That is for absolute temperatures $\vartheta \leqslant 0.35\vartheta_m$, where ϑ_m is the melting temperature of the material.

[4] Notation: We use standard notation of modern continuum mechanics (Gurtin et al., 2010). Specifically: ∇ and Div denote the gradient and divergence with respect to the material point $\mathbf{X}$ in the reference configuration; grad and div denote these operators with respect to the point $\mathbf{x} = \boldsymbol{\chi}(\mathbf{X}, t)$ in the deformed body; a superposed dot denotes the material time-derivative. Throughout, we write $\mathbf{F}^{e-1} = (\mathbf{F}^e)^{-1}$, $\mathbf{F}^{e-\top} = (\mathbf{F}^e)^{-\top}$, etc. We write tr $\mathbf{A}$, sym $\mathbf{A}$, skw $\mathbf{A}$, $\mathbf{A}_0$, and sym$_0\mathbf{A}$ respectively, for the trace, symmetric, skew, deviatoric, and symmetric–deviatoric parts of a tensor $\mathbf{A}$. Also, the inner product of tensors $\mathbf{A}$ and $\mathbf{B}$ is denoted by $\mathbf{A} : \mathbf{B}$, and the magnitude of $\mathbf{A}$ by $|\mathbf{A}| = \sqrt{\mathbf{A} : \mathbf{A}}$.

[5] Also sometimes referred to as the *intermediate* or *relaxed* local space at $\mathbf{X}$.