Equation Chapter 1 Section 1

A COUPLED DISLOCATION-HYDROGEN BASED MODEL OF INELASTIC DEFORMATION

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ABSTRACT

An inelastic model is developed within the thermodynamic framework of Gurtin to describe the hydrogen effect on material deformation. Internal state variables associated with statistically stored dislocations, the concentration of hydrogen, and associated gradients are introduced into the Helmholtz free energy, in addition to the standard variables of elastic strain and temperature. The power expended by microforces related to the hydrogen solutes and concentration gradients is included in the thermodynamics, and these forces are required to satisfy equilibrium conditions at the micro level. The theory is developed for small strains, whereby the total strain is decomposed into the sum of contributions form elasticity, plasticity (dislocation) and hydrogen effects. Thermodynamic restrictions from the dissipation inequality result in the restriction that the stress and microforces are defined as derivatives of the free energy with respect to elastic strain, and hydrogen concentration and its gradient, respectively. Furthermore, a general form for the chemical potential is constructed based upon thermodynamic restrictions. It is a function of the hydrogen concentration and its gradient, and includes the effects of hydrogen on lattice dilatation and dislocation density. Mass balance for the hydrogen results in Fick's law (hydrogen rate is proportional to the flux of hydrogen). The flux is then expressed as the divergence of a function proportional to the gradient of the chemical potential. The energy balance yields a heat conduction equation that includes plastic working as a source term (dissipation) and also the effects of dislocation storage and hydrogen.

The plastic flow rule is based upon the thermally activated motion of dislocations over local barriers, and therefore depends upon the von Mises stress. The strength of the activation barrier depends upon the internal strength of the material through the statistically stored dislocations. These dislocations are stored inversely with their mean free path (which depends upon dislocation spacing) and recover proportionally to their density. In accordance with experimental observations, hydrogen is modeled to reduce the activation energy for dislocation slip and also reduce the dislocation spacing thereby affecting the macroscopically observed flow properties of the material.

1 INTRODUCTION

The present work aims at setting a thermodynamic framework for the description of the hydrogen interactions with deformation. It is well known that hydrogen interacts with hydrostatic stress and this interaction is accounted for in the chemical potential expression through an interaction energy term between hydrostatic stress and lattice dilatation [1]. Hydrogen also interacts with plastic deformation [2] and its effect is demonstrated by the reduction of the strength of barriers to dislocation motion [3]. There is no expression to date that addresses the effect of hydrogen/plasticity interaction on the form of the chemical potential of the solute. Such a contribution to the chemical potential affects the deformation related aspects of the hydrogen transport equations and in turn the hydrogen population development in the presence of trapping at microstructural defects ahead of stress raisers such as notch tips [4].

The interaction of hydrogen with dislocations is another issue that has not been addressed thoroughly as of yet by current constitutive models [5] incorporating the hydrogen effect. It is essential that any continuum theory aiming to describe hydrogen-assisted plastic flow localization it address the fact that hydrogen continues to accumulate preferentially in the area where localization has begun. A new model is needed that clearly simulates this localized response by allowing for dramatic local flow stress reductions due to massive local hydrogen accumulations. Such an approach will require a continuum model that addresses hydrogen assisted recovery and its contribution to the flow stress in conjunction with the competing effect of material hardening due to dislocation multiplication.

To address these micromechanics related issues, we start from a complete continuum thermodynamic viewpoint and we incorporate the hydrogen/deformation interactions as they have been observed and measured experimentally [2].

2 BALANCE LAWS

The theory is based upon the general formalism proposed by Gurtin [6] through which the effects of hydrogen will be coupled with an existing dislocation based plasticity model [7]. In the simplest form of the theory, we introduce two scalar internal variables representing the effects of statistically stored dislocations and hydrogen whose concentration is represented by C (hydrogen atoms per unit volume) or c (hydrogen atoms per solvent atom), where $C = cN_A/V_M$, N_A is Avogadro's number, and V_M is the molar volume of the host lattice.

Since we are not allowing hydrogen to be created or destroyed

$$\frac{d}{dt}\int_V N_L c\,dV + \int_S \mathbf{j}.\mathbf{n}\,ds = 0, \tag{1}$$

where $\mathbf{j}$ is the flux of hydrogen atoms, V is the volume of the region considered, S the bounding surface, $\mathbf{n}$ the outward unit normal, and $N_L = N_A/V_M$. Using the divergence theorem and from the arbitrariness of the volume of integration, one finds the local form as

$$N_L\dot{c} = -\nabla.\mathbf{j}, \tag{2}$$

where a superposed dot denotes time differentiation (d/dt). For dilute solutions and small strains, $\dot{C} = N_L\dot{c}$, and Eq. (2) gives the standard form of Fick's first law

$$\dot{C} = -\nabla.\mathbf{j}. \tag{3}$$

The presence of the hydrogen atoms causes a distortion of the lattice resulting in micro forces or stresses that act over shorter ranges than those from the applied loads. We introduce a microforce ξ that acts on the boundary of a region of the body and is associated with internal and external scalar body forces π and γ. These forces ξ and π represent the effects of neighboring atoms upon the lattice inside the region while γ is the force associated with atom rearrangement within the region. The global balance law that these forces are required to satisfy for equilibrium is of the form

$$\int_S \xi\cdot\mathbf{n}\,ds + \int_V \pi\,dV + \int_V \gamma\,dV = 0. \tag{4}$$

Then the local form of the microforce balance becomes

$$\nabla\cdot\xi + \pi + \gamma = 0. \tag{5}$$

The power delivered to the region by these microforces can be represented by

$$P_{mic} = \int_S (\xi\cdot\mathbf{n})\dot{C}\,dS + \int_V \gamma\dot{C}\,dV. \tag{6}$$

Apart from this external power associated with the microforces, additional power is delivered by the diffusing hydrogen solutes

$$P_{hyd} = -\int_{S} \mu \mathbf{j}.\mathbf{n} dS. \tag{7}$$

Therefore the balance of energy is modified by these additional power contributions and assumes the form

$$\frac{d}{dt}\int_{V} \rho e dV = \int_{V} \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} dV - \int_{S} \mathbf{q}.\mathbf{n} dS + \int_{V} \rho r dV + P_{mic} + P_{hyd} \ , \tag{8}$$

where ρ is the density, e the internal energy, $\boldsymbol{\sigma}$ the stress tensor, $\dot{\boldsymbol{\varepsilon}}$ the strain rate tensor, $\mathbf{q}$ the heat flux, and r internal heat supply. This simply states that the time rate of change of internal energy results from the working of stresses from externally supplied loads minus loss from heat flow through the boundaries plus internal production from radiation, in addition to the power expended by the external microforces and the addition of hydrogen solutes. Substituting the expressions for the external power from Eqs. (6) and (7) into Eq. (8) yields,

$$\frac{d}{dt}\int_{V} \rho e dV = \int_{V} \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} dV - \int_{S} \mathbf{q}.\mathbf{n} dS + \int_{V} \rho r dV + \int_{S} \left(\boldsymbol{\xi}.\mathbf{n}\right) \dot{C} dS + \int_{V} \gamma \dot{C} dV - \int_{V} \mu \mathbf{j}.\mathbf{n} dS. \tag{9}$$

Following standard arguments, one finds the local form of the first law as

$$\rho \dot{e} = \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} + h - \left(\pi - \mu\right) \dot{C} + \boldsymbol{\xi}.\nabla \dot{C} - \mathbf{j} - \nabla \mu, \tag{10}$$

where the heating h is defined to be

$$h = -\nabla . q + \rho r. \tag{11}$$

Recall the second law, which states that the time rate of change of entropy has to be greater than any changes resulting from radiation or heat flux at a particular temperature,

$$\frac{d}{dt}\int_{V} \rho \eta dV \geq \int_{V} \frac{\rho r}{\theta} dV - \int_{S} \frac{\mathbf{q}.\mathbf{n}}{\theta} dS, \tag{12}$$

where η is the entropy density and θ is the temperature. This reduces to the standard local form

$$\rho \theta \dot{\eta} + \theta \nabla . \left(\frac{\mathbf{q}}{\theta}\right) - \rho r \geq 0. \tag{13}$$

Substitution of Eq. (13) into the first law given by Eq. (10) and introduction of the Helmholtz free energy density $\psi = e - \eta \theta$ result in a reduced entropy inequality of the form

$$\rho\left(\dot{\psi} + \eta \dot{\theta}\right) - \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} + \frac{\mathbf{q}}{\theta} \cdot \nabla \theta + \left(\pi - \mu\right) \dot{C} - \boldsymbol{\xi}.\nabla \dot{C} + \mathbf{j}.\nabla \mu \leq 0. \tag{14}$$

Notice that for an isothermal process ($\nabla \theta = 0, \ \dot{\theta} = 0$)

$$\rho \dot{\psi} - \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}} + \left(\pi - \mu\right) \dot{C} - \boldsymbol{\xi}.\nabla \dot{C} + \mathbf{j}.\nabla \mu \leq 0. \tag{15}$$

3 THERMODYNAMIC RESTRICTIONS ON THE CONSTITUTIVE EQUATIONS

Begin with the general assumption that the free energy, entropy, stresses and fluxes depend upon the elastic strain $\boldsymbol{\varepsilon}_e$, the strain associated with statistically stored dislocations ε_{ss}, the temperature, concentration of hydrogen, the chemical potential and their gradients in the form

$$\begin{aligned}
&\psi = \psi\left(\boldsymbol{\varepsilon}_e, \varepsilon_{ss}, \theta, \nabla\theta, C, \nabla C, \mu, \nabla\mu\right),\\
&\eta = \eta\left(\boldsymbol{\varepsilon}_e, \varepsilon_{ss}, \theta, \nabla\theta, C, \nabla C, \mu, \nabla\mu\right),\\
&\boldsymbol{\sigma} = \boldsymbol{\sigma}\left(\boldsymbol{\varepsilon}_e, \varepsilon_{ss}, \theta, \nabla\theta, C, \nabla C, \mu, \nabla\mu\right),\\
&\mathbf{q} = \mathbf{q}\left(\boldsymbol{\varepsilon}_e, \varepsilon_{ss}, \theta, \nabla\theta, C, \nabla C, \mu, \nabla\mu\right),\\
&\mathbf{j} = \mathbf{j}\left(\boldsymbol{\varepsilon}_e, \varepsilon_{ss}, \theta, \nabla\theta, C, \nabla C, \mu, \nabla\mu\right),\\
&\boldsymbol{\xi} = \boldsymbol{\xi}\left(\boldsymbol{\varepsilon}_e, \varepsilon_{ss}, \theta, \nabla\theta, C, \nabla C, \mu, \nabla\mu\right),\\
&\pi = \pi\left(\boldsymbol{\varepsilon}_e, \varepsilon_{ss}, \theta, \nabla\theta, C, \nabla C, \mu, \nabla\mu\right).
\end{aligned} \tag{16}$$

Notice that the chemical potential μ has become a constitutive variable so processes far from equilibrium can be analyzed. Assuming that the total strain rate $\dot{\boldsymbol{\varepsilon}}$ is decomposed into elastic $\dot{\boldsymbol{\varepsilon}}_e$, plastic $\dot{\boldsymbol{\varepsilon}}_p$, and hydrogen-induced $\dot{\boldsymbol{\varepsilon}}_h$ parts, that is, $\dot{\boldsymbol{\varepsilon}} = \dot{\boldsymbol{\varepsilon}}_e + \dot{\boldsymbol{\varepsilon}}_p + \dot{\boldsymbol{\varepsilon}}_h$, and substituting Eqs. (16) into the dissipation inequality (14), one finds

$$\begin{aligned}
&\left(\boldsymbol{\sigma} - \rho\frac{\partial\psi}{\partial\boldsymbol{\varepsilon}_e}\right) : \dot{\boldsymbol{\varepsilon}}_e - \rho\left(\eta + \frac{\partial\psi}{\partial\theta}\right)\dot{\theta} - \rho\frac{\partial\psi}{\partial\varepsilon_{ss}}\dot{\varepsilon}_{ss} - \left(\rho\frac{\partial\psi}{\partial C} + \pi - \mu\right)\dot{C} - \left(\rho\frac{\partial\psi}{\partial\nabla C} - \boldsymbol{\xi}\right).\nabla\dot{C}\\
&-\rho\frac{\partial\psi}{\partial\mu}\dot{\mu} - \rho\frac{\partial\psi}{\partial\nabla\mu}\cdot\nabla\dot{\mu} + \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}}_p + \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}}_h - \frac{1}{\theta}\mathbf{q}.\nabla\theta - \mathbf{j}.\nabla\mu \geq 0.
\end{aligned} \tag{17}$$

Standard arguments to ensure that the entropy inequality is not violated provide

$$\frac{\partial\psi}{\partial\mu} = \mathbf{0}, \frac{\partial\psi}{\partial\nabla\mu} = \mathbf{0}, \boldsymbol{\sigma} = \rho\frac{\partial\psi}{\partial\boldsymbol{\varepsilon}_e}, \eta = -\frac{\partial\psi}{\partial\theta}, \frac{\partial\psi}{\partial\nabla\theta} = 0\ , \boldsymbol{\xi} = \rho\frac{\partial\psi}{\partial\nabla C}, \mu - \pi = \rho\frac{\partial\psi}{\partial C}, \tag{18}$$

and by defining the internal strength of the material κ as

$$\kappa = \frac{\partial\psi}{\partial\varepsilon_{ss}}, \tag{19}$$

one finds that the dissipation inequality reduces to

$$\boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}}_p + \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}}_h - k\dot{\varepsilon}_{ss} - \frac{1}{\theta}\mathbf{q}.\nabla\theta - \mathbf{j}.\nabla\mu \geq 0. \tag{20}$$

Now combine the expression for π from Eq. (18) with the microforce balance in Eq. (5) to find

$$\mu = \rho\frac{\partial\psi}{\partial c} - \nabla.\left[\rho\frac{\partial\psi}{\partial\nabla C}\right] - \gamma. \tag{21}$$

Fluxes $\mathbf{q}$ and $\mathbf{j}$ are assumed linear in the gradient of temperature and chemical potential, respectively, i.e.,

$$\mathbf{q} = -A\nabla\theta\ ,\ \mathbf{j} = -B\nabla\mu. \tag{22}$$

Then, with the assumption that $\gamma = 0$ the energy balance Eq. (10) reduces to

$$\begin{aligned}
&\rho c_p\dot{\theta} - \rho\theta\frac{\partial}{\partial\theta}\left(\frac{\partial\psi}{\partial C}\right)\dot{C} - \rho\theta\left(\frac{\partial\psi}{\partial\nabla C}\right).\nabla\dot{C} = \nabla.\left(\mathbf{A}\nabla\theta\right) + \left(\mathbf{B}\nabla\mu\right).\nabla\mu + \rho r\\
&+\rho\theta\left[\frac{\partial}{\partial\theta}\left(\frac{\boldsymbol{\sigma}}{\rho}\right) : \dot{\boldsymbol{\varepsilon}}_e + \frac{\partial}{\partial\theta}\left(\frac{\kappa}{\rho}\right)\dot{\varepsilon}_{ss}\right] + \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}}_p + \boldsymbol{\sigma} : \dot{\boldsymbol{\varepsilon}}_h - k\dot{\varepsilon}_{ss},
\end{aligned} \tag{23}$$

where $c_p = \theta\partial\eta/\partial\theta$.

4 CONSTITUTIVE EQUATIONS

A specific form for the free energy dependence upon independent variables is now considered. In general, the free energy is assumed to have a quadratic dependence upon variables that are elastic strain like, hence

$$\rho\psi = \bar{\psi}\left(\boldsymbol{\varepsilon}_e, \varepsilon_{ss}, C, \nabla C\right) = \frac{1}{2}\boldsymbol{\varepsilon}_e : \mathbf{L} : \boldsymbol{\varepsilon}_e + \frac{1}{2}\kappa\varepsilon_{ss} + z\left(C\right), \tag{24}$$

where $\mathbf{L}$ is the tensor of the elastic moduli; and $z\left(C\right)$ is composed of a "coarse-grain" part $f\left(C\right)$, a part associated with the hydrogen-induced dilatation $\boldsymbol{\varepsilon}_h = \left(\varepsilon_h/3\right)\boldsymbol{\delta}$ of the lattice with $\boldsymbol{\delta}$ being the identity tensor, and a double-well potential whose wells define the hydrogen phase:

$$\begin{aligned} z\left(C\right) &= f\left(C\right) + \frac{E}{9\left(1-\nu\right)}\varepsilon_h^2 + \frac{1}{2}\alpha\left(\nabla C \cdot \nabla C\right) \\ &= f\left(C\right) + \frac{E}{9\left(1-\nu\right)}\left[\frac{\lambda}{\rho}\left(C - C_0\right)\right]^2 + \frac{1}{2}\alpha\left(\nabla C \cdot \nabla C\right). \end{aligned} \tag{25}$$

In Eq. (25), E and ν are Young's modulus and Poisson's ratio respectively, λ is the dilatation induced by a hydrogen solute in multiples of the atomic volume of the host lattice, C_0 is the stress-free initial concentration of hydrogen, and α is a proportionality constant. Then it follows from Eq. (18) that

$$\begin{aligned} &\boldsymbol{\sigma} = \rho\frac{\partial\psi}{\partial\boldsymbol{\varepsilon}_e} = \mathbf{L} : \boldsymbol{\varepsilon}_{\mathbf{e}}\ ,\ \boldsymbol{\xi} = \rho\frac{\partial\psi}{\partial\nabla C} = \alpha\nabla C\ ,\ \pi = -\nabla.\left(\rho\frac{\partial\psi}{\partial\nabla C}\right) = -\alpha\nabla^2 C, \\ &\mu = \rho\frac{\partial\psi}{\partial C} - \nabla.\left(\rho\frac{\partial\psi}{\partial\nabla C}\right) = f'\left(C\right) - \boldsymbol{\sigma} : \frac{\partial\boldsymbol{\varepsilon}_p}{\partial C} - \frac{\lambda}{\rho}\frac{tr\boldsymbol{\sigma}}{3} - \alpha\nabla^2 C + \frac{2E}{9\left(1-\nu\right)}\left(\frac{\lambda}{\rho}\right)^2\left(C - C_0\right). \end{aligned} \tag{26}$$

Finally, combining the mass balance for hydrogen Eq. (3) with Eq. (22) yields

$$\dot{C} = -\nabla.\mathbf{j} = -\nabla.\left(\mathbf{B}\nabla\mu\right) \tag{27}$$

in which we assume $\mathbf{B} = \left(DC/k\theta\right)\boldsymbol{\delta}$ with D and k being the diffusion and Boltzmann's constants, respectively. For dilute solutions, a form compatible with standard metallurgical thermodynamic theory of solute impurities is

$$f\left(C\right) = k\theta\left[c\ln c + \left(1-c\right)\ln\left(1-c\right)\right]. \tag{28}$$

To complete the model it is necessary to specify expression for the plastic flow $\dot{\boldsymbol{\varepsilon}}_p$ and the evolution of the statistically stored dislocations ρ_{ss}, since we assume the elastic strain stored in the lattice from the presence of these defects is given as $\varepsilon_{ss} = \mu b\sqrt{\rho_{ss}}$ [7]. The form of these equations is given by

$$\begin{aligned} \dot{\boldsymbol{\varepsilon}}_p &= f\sinh\left\{\left(q\left(C\right)\frac{\left|\boldsymbol{\sigma}'\right|}{Y+\kappa} - 1\right)^n\right\}\frac{\boldsymbol{\sigma}'}{\left|\boldsymbol{\sigma}'\right|}, \\ \dot{\rho}_{ss} &= \left(k_1\left(C\right)\sqrt{\rho_{ss}} - k_2\left(C\right)\rho_{ss}\right)\left|\dot{\boldsymbol{\varepsilon}}_p\right|, \end{aligned} \tag{29}$$

where $\boldsymbol{\sigma}'$ is the stress deviator, $\left|\bullet\right|$ denotes effective measure of tensor $\bullet$, f and Y are parameters related to a reference strain rate and yield stress, $k_1\left(C\right)$ and $k_2\left(C\right)$ are hydrogen dependent hardening and recovery parameters, respectively [7], and $q\left(C\right)$ describes the effect of hydrogen in lowering the activation energy for dislocation slip. Hardening parameter $k_1(C)$ reflects the reduction in statistically stored dislocation spacing from the presence of hydrogen [3] and the associated shortening of the mean free path for dislocation slip.

5 CONCLUSIONS

Within the thermodynamic formalism proposed by Gurtin [6], a model of inelastic deformation that accounts for the interaction between dislocation slip and hydrogen has been developed. The small strain version of the model assumes the decomposition of the total strain into the sum of elastic, plastic (dislocation) and hydrogen parts. The plastic strain rate is governed by thermally activated motion of dislocations and depends upon the internal strength of the crystal which evolves based upon a dislocation storage with a hardening and recovery format. The effects of hydrogen on dislocation plasticity are accounted for by the decrease in the activation barrier for dislocation slip and the reduction of the mean free path for dislocation storage. The balance of energy yields a hydrogen dependent heat conduction equation that includes the effects of dislocation storage as well as the effects of hydrogen on material deformation. Restrictions imposed by the second law provide a form for the chemical potential of the hydrogen solute that depends upon the hydrogen concentration and gradients, the hydrogen-induced distortion of the lattice, and the interaction of hydrogen with dislocations. Implementation of the model into finite element codes is in progress.

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REFERENCES

1. Li, J. C. M., Oriani, R. A. and Darken, L. S., The thermodynamics of stressed solids. *Z. Physik Chem. Neue Folge*, 49, 271-291, 1966.
2. Birnbaum, H. K. and Sofronis, P., Hydrogen-enhanced localized plasticity-a mechanism for hydrogen related fracture, Mater. Sci. Eng. A176, 191-202, 1994.
3. Sofronis, P. and Birnbaum, H. K., Mechanics of the hydrogen-dislocation-impurity interactions--I. Increasing shear modulus, J. Mech. Phys. Solids, 43, 49-90, 1995.
4. Taha, A. and Sofronis, P., A micromechanics approach to the study of hydrogen transport and embrittlement, Engineering Fracture Mechanics, 68, 803-837, 2001.
5. Sofronis, P., Liang, Y., and Aravas, N., Hydrogen induced shear localization of the plastic flow in metals and alloys, European Journal of Mechanics A –Solids, 20, 857-872, 2001.
6. Gurtin, M.E., Generalized Ginzburg-Landau and Cahn-Hilliard equations based on a microforce balance, Physica D, 92, 178-192, 1996
7. Bammann, D.J., A model of crystal plasticity containing a natural length scale. Mat. Sci. Eng. A309-310, 406-410, 2001.