

Thermodynamics and Multi-physical Model for Application to the Effect of Severe Environment on Metallic Alloys

K. Saliya, B. Panicaud, C. Labergere

Abstract. In this paper, we have formulated a fully coupled thermo-elasto-visco-plastic-damage theory, which includes both kinematic and isotropic hardening, and takes also into account the diffusion of several species in metals. This theory is based on the thermodynamics of irreversible processes under small strain hypothesis. Each specie is supposed to diffuse in both lattice and trapping sites. In order to take correctly into account of different coupling effects, the diffusion fluxes vectors depend not only on the gradient of chemical potential, but also on the gradient of temperature (thermodiffusion) and on the gradient of pressure (barodiffusion). The heat flux also depends not only on the gradient of temperature, but also on the chemical potential gradient of each specie, according to the thermodynamics of irreversible processes. This model is implemented into Abaqus/Standard using the Uel user subroutine. An application is made for the diffusion of hydrogen in TA6V after welding.

1 Introduction

In various industrial sectors, some metal parts of more or less complex shape have to be carefully dimensioned to resist with time to thermo-mechanical stresses, but also to a more or less aggressive environment (aqueous or gaseous media). When a metal structure must withstand thermo-mechanical stresses over very long periods, the problem arises to take also into account the degradation of these mechanical properties by the presence of gas such as hydrogen, which can diffuse into the material and weaken it. The presence of oxygen could also be considered, which generally oxidizes its surface. The degradation of materials subjected to such aggressive environments put significant challenge for engineering. To achieve such a goal, it is necessary to model and predict at least the diffusion of hydrogen and/or oxygen, which generates indirectly a degradation of mechanical properties, in order to improve the reliability and predictivity of models.

For hydrogen, its effects on mechanical response are now well known. Metals and alloys are degraded in presence of hydrogen (Bernstein, 1970; Oriani, 1978; Hirth, 1980; Delafosse and Magnin, 2001; Sofronis et al., 2001). One of this phenomenon is known as hydrogen embrittlement. Embrittlement by hydrogen is explained by a great number of theories, but two of them are the most developed: hydrogen enhanced decohesion (HEDE) and hydrogen locally enhanced plasticity (HELP). On one hand, HEDE theory explains that interstitial hydrogen lowers the cohesive strength by dilatation of the atomic lattice leading to lower the fracture energy. This implies that hydrogen reduces the cohesion (Oriani and Josephic, 1974; Gerberich and Chen, 1975). On the other hand, HELP theory is characterized by atomic hydrogen that favors or enhances the mobility of dislocations through an elastic shielding effect in some specific crystallographic planes at the crack tip, causing locally a decrease of shear strength (Birnbaum and Sofronis, 1994; Lufrano et al., 1996; Lufrano et al., 1998; Sofronis et al., 2001). Several authors have proposed models for the study of hydrogen embrittlement near a crack tip (Lufrano et al., 1998; Sofronis et al., 2001; Taha and Sofronis, 2001; Di Leo and Anand, 2013; Diaz et al., 2016; etc.). All these models consider two kinds of sites for hydrogen diffusion: normal interstitial lattice sites and microstructural trapping sites such as dislocation core, grain boundary, and interfaces between the matrix and various second-phase particles. Most of these models use the postulate of Oriani (1970): “within a continuum-level material point, and for a specific range of trap binding energies, the microstructure affects the local distribution of hydrogen in a manner such that the population of hydrogen in trapping sites is always in equilibrium with the population associated with normal interstitial lattice sites”.

The existing models, although allowing studying the effects of hydrogen diffusion on the mechanics and reciprocally, are not fully based on the thermodynamics of irreversible processes. The only model, which is based on the thermodynamics of irreversible processes, is the one of Di Leo et al. (2013). These authors have formulated a thermo-mechanically coupled-theory, which accounts for diffusion of hydrogen and large elastic-plastic deformations of metals. Their theory accounts for the trapping of hydrogen within a fully thermodynamically-consistent framework.

In the present article, as Di Leo et al. (2013), we will base our developments on the thermodynamics of irreversible processes and develop a constitutive model taking into account the couplings between volume diffusion, chemical reactions at surface, and thermo-mechanical behavior including ductile damage. This model includes both kinematic and isotropic hardening in the material. At our knowledge, this is the first time that a coupled theory for species diffusion and thermo-elasto-visco-plastic model takes into account simultaneously ductile damage and both kinematic and isotropic hardenings. The model supposes the presence of several chemical species, such as hydrogen from the environment. In this case, the flux of the considered specie n may depend on the gradient of the chemical potentials of the others species m .

The elasto-visco-plastic coupled model, taking into account different hardenings (isotropic and kinematic) in the material and strongly coupled to damage and to temperature has been widely studied (e.g. Saanouni et al., 2011; Saanouni, 2012). This model is built on a thermodynamics framework, with temperature as external state variable to fully couple mechanics with temperature effects. Ductile isotropic damage is also considered by the use of a Lemaitre and Chaboche model (Lemaitre and Chaboche, 1985). Therefore, we base our modeling on this elasto-visco-plastic coupled model and naturally extend it to diffusion of species.

A model for hydrogen diffusion, which is the first stage of our study, is eventually implemented in Abaqus/Standard to study hydrogen diffusion in TA6V after welding and submitted to a long-time severe environment.

2 Thermodynamics Modeling

To develop the thermo-mechanical-damage and diffusion coupled model by taking into account the kinematic and isotropic hardenings, we base our theory on the thermodynamics of irreversible processes with state variables. We assume the small strain hypothesis. The model is an extension of the fully coupled thermo-elasto-visco-plastic model including ductile damage and both kinematic and isotropic hardening (e.g. Lemaitre and Chaboche, 1985; Lemaitre, 1992; Saanouni et al., 2011; Saanouni, 2012; etc.). Therefore, we introduce two “external” state variables: $(\underline{\varepsilon}, \underline{\sigma})$ for total strain tensor and Cauchy stress tensor; (T, s_e) for absolute temperature and specific entropy. We introduce also “internal” state variables extended to the diffusion case: $(\underline{\varepsilon}^e, \underline{\sigma})$ for elastic strain tensor and Cauchy stress tensor; $(\vec{q}, \vec{\nabla}T)$ for heat flux vector and its conjugate force the temperature gradient; $(\underline{\alpha}, \underline{X})$ for the back-strain and back-stress deviator tensors that describe the kinematic hardening; (r, R) for equivalent plastic driving strain and stress that describe the isotropic hardening; (D, Y) for isotropic damage and its conjugate force, which also corresponds to a driving damage through strain energy release rate (Lemaitre, 1992).

For the diffusion, we suppose that several chemical species such as hydrogen can diffuse within the material. For a given specie n , it is assumed that it has two “levels” of diffusion: diffusion in normal interstitial lattice sites (L) and “diffusion” in trapping sites (T) at microstructural defects generated by plastic strain such as dislocation. We introduce therefore two concentrations (c_n^L for lattice sites and c_n^T for trapping sites) and two chemical potentials (μ_n^L for lattice sites and μ_n^T for trapping sites) for each specie n . Therefore, we introduce (c_i^L, μ_i^L) and (c_i^T, μ_i^T) as internal state variables describing the diffusion phenomena of each specie i in the model for both lattice and trapping sites.

2.1 Free Energy Specialization

The state potential is classically taken as Helmholtz free energy ψ as a function of the different state variables, $\psi = \psi(\underline{\varepsilon}^e, \underline{\alpha}, r, D, T, c_i^L, c_i^T)$.

To build this free energy, we suppose that elasticity-temperature coupling, elasticity-concentration coupling and damage-plasticity coupling are strong. The other couplings are supposed to be weak (meaning that only the coefficients depend on the different variables). We consider therefore the free energy as a sum of three energies: elastic, plastic and diffusion energy.

$$\rho\psi(\underline{\varepsilon}^e, \underline{\alpha}, r, D, T, c_i^L, c_i^T) = \begin{pmatrix} \rho\psi^e(\underline{\varepsilon}^e, D, T, c_i^L, c_i^T) + \rho\psi^p(\underline{\alpha}, r, D, T, c_i^L, c_i^T) \\ + \rho\psi^{dif}(\underline{\alpha}, r, D, T, c_i^L, c_i^T) \end{pmatrix} \quad (1)$$

Note that the kind of damage to be modeled in this paper is ductile damage. The various defects responsible for this ductile damage are the inclusions, the dislocations stacks, the grain boundaries, the particles of additive elements in the alloy, and the dislocation obtained by heat treatment.

In the case of small strain hypothesis and isotropic case, using scalar argument (representation theorem (Boehler 1978)), we define:

$$\rho\psi^e(\underline{\varepsilon}^e, D, T, c_i^L, c_i^T) = \begin{cases} \frac{(1-D)}{2} \left(\lambda (\underline{\varepsilon}^e : \underline{1})^2 + 2\mu \underline{\varepsilon}^e : \underline{\varepsilon}^e \right) \\ -3K\vartheta(T-T_0)\sqrt{1-D}\underline{\varepsilon}^e : \underline{1} - \rho C_v \frac{(T-T_0)^2}{2T_0} \\ -\sum_i 3K\beta(c_i^L - c_{i0}^L)\sqrt{1-D}\underline{\varepsilon}^e : \underline{1} - \sum_i 3K\beta(c_i^T - c_{i0}^T)\sqrt{1-D}\underline{\varepsilon}^e : \underline{1} \end{cases} \quad (2)$$

$$\rho\psi^p(\underline{\alpha}, r, D, T, c_i^L, c_i^T) = \frac{1}{3}C(1-D)\underline{\alpha} : \underline{\alpha} + \frac{1}{2}(1-D)Qr^2 \quad (3)$$

$$\rho\psi^{dif}(\underline{\alpha}, r, D, T, c_i^L, c_i^T) = \begin{cases} \sum_i \left[\mu_{i0}^L c_i^L + RTN^L \left[\theta_i^L \ln \theta_i^L + (1-\theta_i^L) \ln(1-\theta_i^L) \right] \right] \\ + \sum_i \left[\mu_{i0}^T c_i^T + RTN^T \left[\theta_i^T \ln \theta_i^T + (1-\theta_i^T) \ln(1-\theta_i^T) \right] \right] \end{cases} \quad (4)$$

Where ρ is the material density, λ and μ are the Lamé's constants for isotropic elasticity, K the compressibility or bulk modulus ($K = (3\lambda + 2\mu)/3$), C_v the specific heat coefficient, T_0 the reference temperature, Q and C are respectively the isotropic and kinematic hardening modulus. ϑ and β are respectively the thermal and the chemical expansion coefficient. As Di Leo and Anand (2013), in equation (2) we suppose that the amount of chemical expansion caused by the trapping specie is the same as the one caused by the lattice specie, hence the same β . N^L and N^T are respectively the number of moles of lattice and trapping sites per unit of reference volume, θ_i^L and θ_i^T are respectively the occupancy fraction of the lattice and trapping sites and are directly related to its corresponding concentration by: $\theta_i^L = c_i^L/N^L$ and $\theta_i^T = c_i^T/N^T$.

Note that in equation (2), damage is introduced through the elastic strain, and we suppose that damage has no direct influence on the thermal and chemical state variables. Hence, damage appears in the expression (2) with a term $(1-D)$ before the elastic strain energy density and $\sqrt{1-D}$ before the thermal and chemical expansion terms.

The free energy we define is therefore a generalization of the thermo-elasto-visco-plastic energy function with isotropic damage (Saanouni et al., 2011), extended to the diffusion.

2.2 State Relations Specification

Knowing the explicit expression of the Helmholtz free energy, we can explicit the "state relations".

In several works, the deformation due to diffusion is defined separately (e.g.: Sofronis et al., 2001; Díaz et al., 2016; etc.). In the present work, based on the thermodynamics of irreversible processes, this deformation is directly included in the expression of Cauchy stress tensor as shows in equation (5):

$$\underline{\sigma} = \rho \frac{\partial \psi}{\partial \underline{\varepsilon}^e} = \begin{cases} (1-D) \left(\lambda (\underline{\varepsilon}^e : \underline{1}) \underline{1} + 2\mu \underline{\varepsilon}^e \right) - 3K\vartheta \sqrt{(1-D)}(T-T_0)\underline{1} \\ -3K\beta \sum_i (c_i^L - c_{i0}^L) \sqrt{1-D} \underline{1} - 3K\beta \sum_i (c_i^T - c_{i0}^T) \sqrt{1-D} \underline{1} \end{cases} \quad (5)$$

The specific entropy takes now into account the diffusion effects as in equation (6):

$$s_e = -\frac{\partial \Psi}{\partial T} = \begin{cases} \frac{3}{\rho} K \vartheta \sqrt{1-D} \underline{\underline{\varepsilon}}^e : \underline{\underline{1}} + C_v \frac{(T-T_0)}{T_0} \\ -\frac{1}{\rho} \sum_i \left[RN^L \left[\theta_i^L \ln \theta_i^L + (1-\theta_i^L) \ln(1-\theta_i^L) \right] \right] \\ -\frac{1}{\rho} \sum_i \left[RN^T \left[\theta_i^T \ln \theta_i^T + (1-\theta_i^T) \ln(1-\theta_i^T) \right] \right] \end{cases} \quad (6)$$

Only back-stress and plastic driving stress are not explicitly function of diffusion.

$$\text{Back-stress deviator: } \underline{\underline{X}} = \rho \frac{\partial \Psi}{\partial \underline{\underline{\alpha}}} = \frac{2}{3} C (1-D) \underline{\underline{\alpha}} \quad (7)$$

$$\text{Plastic driving stress: } R = \rho \frac{\partial \Psi}{\partial r} = Q (1-D) r \quad (8)$$

Damage conjugate force expression also change to take into account the diffusion effects:

$$Y = -\rho \frac{\partial \Psi}{\partial D} = \begin{cases} \frac{1}{2} \lambda \left(\underline{\underline{\varepsilon}}^e : \underline{\underline{1}} \right)^2 + \mu \underline{\underline{\varepsilon}}^e : \underline{\underline{\varepsilon}}^e - \frac{3K\vartheta(T-T_0)}{2\sqrt{(1-D)}} \underline{\underline{\varepsilon}}^e : \underline{\underline{1}} + \frac{1}{3} C \underline{\underline{\alpha}} : \underline{\underline{\alpha}} + \frac{1}{2} Q r^2 \\ -\frac{(3K\beta)}{2\sqrt{(1-D)}} \sum_i \left[(c_i^L - c_{i0}^L) + (c_i^T - c_{i0}^T) \right] \underline{\underline{\varepsilon}}^e : \underline{\underline{1}} \end{cases} \quad (9)$$

Contrarily to other works, which are not based on the thermodynamics of irreversible processes (ex: Sofronis et al., 2001; Díaz et al., 2016; etc.), the influence of the mechanical state on the diffusion of the specie n here is explicitly related to elastic strain tensor and not to Cauchy stress tensor through chemical potentials expressions (equations (10) and (11)).

Chemical potential for lattice sites is for example:

$$\mu_i^L = \rho \frac{\partial \Psi}{\partial c_i^L} = \mu_{i0}^L + RT \ln \left(\frac{\theta_i^L}{1-\theta_i^L} \right) - 3K\beta \sqrt{1-D} \underline{\underline{\varepsilon}}^e : \underline{\underline{1}} \quad (10)$$

Whereas chemical potential for trapping sites is:

$$\mu_i^T = \rho \frac{\partial \Psi}{\partial c_i^T} = \mu_{i0}^T + RT \ln \left(\frac{\theta_i^T}{1-\theta_i^T} \right) - 3K\beta \sqrt{1-D} \underline{\underline{\varepsilon}}^e : \underline{\underline{1}} \quad (11)$$

2.3 Clausius-Duhem Dissipation Inequality

In the following subsections, we analyze the dissipations. To take into account the diffusion effects, the heat flux \vec{q} has also to be modified according to Vidal theory (Vidal et al., 1994):

$\vec{q} \rightarrow \vec{q} - \sum_i (\mu_i^L \vec{J}_i^L + \mu_i^T \vec{J}_i^T)$, where \vec{J}_i^L and \vec{J}_i^T are respectively the diffusion flux in lattice and trapping sites. This modifies the internal energy balance and the entropy balance in these terms:

Internal energy balance:

$$\rho \dot{e} = \underline{\underline{\sigma}} : \underline{\underline{\dot{\varepsilon}}} - \vec{\nabla} \cdot \vec{q} + \pi + \vec{\nabla} \cdot \sum_i (\mu_i^L \vec{J}_i^L + \mu_i^T \vec{J}_i^T) \quad (12)$$

Entropy balance:

$$\rho \dot{s}_e = -\frac{1}{T} \vec{\nabla} \cdot \vec{q} + \frac{\vec{q}}{T^2} \cdot \vec{\nabla} T + \frac{\pi}{T} + \frac{1}{T} \vec{\nabla} \cdot \left(\sum_i (\mu_i^L \vec{J}_i^L + \mu_i^T \vec{J}_i^T) \right) - \left(\frac{\sum_i (\mu_i^L \vec{J}_i^L + \mu_i^T \vec{J}_i^T)}{T^2} \right) \cdot \vec{\nabla} T, \quad (13)$$

with π being the body heat source. With these modifications in the internal energy balance and in the entropy balance, we obtain the generalized Clausius-Duhem dissipation inequality in the following form, with $\underline{\dot{\epsilon}} = \underline{\dot{\epsilon}}^e + \underline{\dot{\epsilon}}^p$:

$$\Phi = \begin{pmatrix} \left(\underline{\sigma} - \rho \frac{\partial \psi}{\partial \underline{\epsilon}^e} \right) : \underline{\dot{\epsilon}}^e + \underline{\sigma} : \underline{\dot{\epsilon}}^p - \rho \left(s_e + \frac{\partial \psi}{\partial T} \right) \dot{T} - \rho \frac{\partial \psi}{\partial \underline{\alpha}} : \underline{\dot{\alpha}} - \rho \frac{\partial \psi}{\partial r} \dot{r} - \rho \frac{\partial \psi}{\partial D} \dot{D} \\ - \rho \sum_i \frac{\partial \psi}{\partial c_i^L} \dot{c}_i^L - \rho \sum_i \frac{\partial \psi}{\partial c_i^T} \dot{c}_i^T - \frac{\vec{q}}{T} \cdot \vec{\nabla} T + \left(\frac{\sum_i (\mu_i^L \vec{J}_i^L + \mu_i^T \vec{J}_i^T)}{T} \right) \cdot \vec{\nabla} T \geq 0 \end{pmatrix} \quad (14)$$

Using the state relations, the residual inequality resulting from the Clausius-Duhem dissipation inequality becomes the sum of mechanical, thermal and diffusion dissipation:

$$\Phi = \Phi^m + \Phi^{th} + \Phi^{dif} \geq 0 \quad (15a)$$

$$\Phi^m = \underline{\sigma} : \underline{\dot{\epsilon}}^p - \underline{X} : \underline{\dot{\alpha}} - R\dot{r} + Y\dot{D} \quad (15b)$$

$$\Phi^{th} = -\frac{\vec{q}}{T} \cdot \vec{\nabla} T + \left(\frac{\sum_i (\mu_i^L \vec{J}_i^L + \mu_i^T \vec{J}_i^T)}{T} \right) \cdot \vec{\nabla} T \quad (15c)$$

$$\Phi^{dif} = -\sum_i (\mu_i^L \dot{c}_i^L + \mu_i^T \dot{c}_i^T) \quad (15d)$$

The different dissipations have now to be analyzed separately in order to derive the flux variables $(\underline{\dot{\epsilon}}^p, \underline{\dot{\alpha}}, \dot{r}, \dot{D}, \vec{q}/T, \dot{c}_i^L, \dot{c}_i^T)$.

2.4 Mechanical Equations

For the mechanical dissipation, the derived equations from our model are those already described by many authors (e.g. Lemaitre, 1992; Saanouni et al., 1994). We remind here some equations. For more information, the reader can refer to the specified references.

Yield function f is defined together with plastic potential F , from which the evolution equations are derived:

$$f(\underline{\sigma}, \underline{X}, R; D, T) = \frac{J_2(\underline{\sigma} - \underline{X})}{\sqrt{1-D}} - \frac{R}{\sqrt{1-D}} - \sigma_Y \leq 0 \quad (16)$$

$$F(\underline{\sigma}, \underline{X}, R; D; T) = f + \frac{a}{2C(1-D)} J_2^2(\underline{X}) + \frac{bR^2}{2Q(1-D)} + \frac{S}{(s+1)(1-D)^\beta} \left[\frac{\langle Y - Y_0 \rangle}{S} \right]^{(s+1)} \quad (17)$$

Both the yield function and the plastic potential are closed convex functions of the stress-like variables $\underline{\sigma}$, \underline{X} and R , with D and T playing the role of parameters (Saanouni et al., 1994; Saanouni and Chaboche, 2003). σ_Y is the initial size of the Mises yield function, b and a are material coefficients describing the nonlinear isotropic and

kinematic hardening respectively, S , s , Y_0 and β are material coefficients characterizing the ductile damage evolution (Lemaitre, 1992; Saanouni et al., 1994). Application of the generalized normality leads to constitutive equations:

$$\underline{\dot{\varepsilon}}^p = \dot{\delta} \frac{\partial f}{\partial \underline{\sigma}} = \dot{\delta} \frac{3}{2} \frac{1}{\sqrt{1-D}} \frac{\underline{S} - \underline{X}}{J_2(\underline{\sigma} - \underline{X})} = \dot{\delta} \underline{n} \quad (18)$$

$$\underline{\dot{\alpha}} = -\dot{\delta} \frac{\partial F}{\partial \underline{X}} = \dot{\delta} (\underline{n} - a\underline{\alpha}) = \underline{\dot{\varepsilon}}^p - a\dot{\delta} \underline{\alpha} \quad (19)$$

$$\dot{r} = -\dot{\delta} \frac{\partial F}{\partial R} = \dot{\delta} \left(\frac{1}{\sqrt{1-D}} - br \right) \quad (20)$$

$$\dot{D} = \frac{\dot{\delta}}{(1-D)^\beta} \left[\frac{\langle Y - Y_0 \rangle}{S} \right]^s \quad (21)$$

$$\underline{n} = \frac{3}{2} \frac{1}{\sqrt{1-D}} \frac{\underline{S} - \underline{X}}{J_2(\underline{\sigma} - \underline{X})}, \quad (22)$$

where \underline{S} is the deviatoric part of the Cauchy stress tensor and the back-stress \underline{X} is a purely deviatoric stress tensor as mentioned above. \underline{n} is a deviatoric tensor which stands for the outward normal to the yield surface in the tress space. It has been shown that the different constitutive equations are valid for both time dependent and time independent plasticity (Saanouni et al., 1994). The only difference is the form of the Lagrange multiplier $\dot{\delta}$. For time dependent flow or visco-plasticity, the Lagrange multiplier is postulated equal to:

$$\frac{\dot{\delta}}{\sqrt{1-D}} = \dot{\delta}_{vp} = \left\langle \frac{f}{k_v} \right\rangle^n, \quad (23)$$

where k_v and n characterize the material viscosity. For time independent plasticity the plastic multiplier is derived from the consistency condition (Saanouni et al., 1994; Saanouni and Chaboche, 2003).

As stated previously at the beginning of this paragraph, in the present work, we take into account the diffusion of species in material. Indeed, hydrogen diffusion for example in metals or alloys induces softening (Sofronis et al., 2001). To model this effect of hydrogen, these authors express the local flow stress as a function of the total concentration of hydrogen C_H in metal and equivalent plastic strain ε^p :

$$\sigma_Y(\varepsilon^p, C_H) = [(\xi - 1)C_H + 1] \sigma_0 \left(1 + \varepsilon^p / \varepsilon_0 \right)^{1/m} \quad (24)$$

With σ_0 the initial yield stress in absence of hydrogen, ε_0 the initial yield strain in absence of hydrogen, m the hardening exponent, with the parameter ξ that is supposed to be less than unity.

In the present model, we suppose also that all species, which diffuse within the material have the same effects as hydrogen and we express σ_Y as function of the total concentration of all species C_i :

$$\sigma_Y(C_i) = [(\xi - 1)C_i + 1] \sigma_{Y_0} \quad (25)$$

With σ_{Y_0} the initial yield stress in absence of hydrogen. The plastic effect in equation (24) is already taken into account in our model by the plastic driving stress R .

2.5 Thermal Equations

Thermal dissipation analysis allows expliciting the general heat equation governing the temperature evolution including the mechanical dissipation in visco-plastic flow, hardening, damage and diffusion dissipation. To establish this equation, on one hand, we express entropy as function of the different state variables. The time variation of entropy and the use of state relation of entropy ($s_e = -\partial\psi/\partial T$) leads to:

$$\rho T \dot{s}_e = -T \left(\frac{\partial \underline{\sigma}}{\partial T} : \underline{\dot{\varepsilon}}^e + \frac{\partial \underline{X}}{\partial T} : \underline{\dot{\alpha}} + \frac{\partial R}{\partial T} \dot{r} - \frac{\partial Y}{\partial T} \dot{D} + \sum_i \frac{\partial \mu_i^L}{\partial T} \dot{c}_i^L + \sum_i \frac{\partial \mu_i^T}{\partial T} \dot{c}_i^T \right) - \rho T \frac{\partial^2 \psi}{\partial T^2} \dot{T} \quad (26)$$

On the other hand, using the first principle of thermodynamics (12), with $e = \psi + Ts_e$, we obtain:

$$\rho T \dot{s}_e = \underline{\sigma} : \underline{\dot{\varepsilon}}^p - \underline{X} : \underline{\dot{\alpha}} - R \dot{r} + Y \dot{D} - \vec{\nabla} \cdot \vec{q} - \sum_i (\mu_i^L \dot{c}_i^L + \mu_i^T \dot{c}_i^T) + \vec{\nabla} \cdot \sum_i (\mu_i^L \vec{J}_i^L + \mu_i^T \vec{J}_i^T) + \pi \quad (27)$$

Equality between equations (26) and (27) give the generalized heat equation in a thermo-elasto-inelastic-damaging solid coupled with diffusion:

$$\rho C_v \dot{T} = \begin{pmatrix} \underline{\sigma} : \underline{\dot{\varepsilon}}^p - \underline{X} : \underline{\dot{\alpha}} - R \dot{r} + Y \dot{D} - \vec{\nabla} \cdot \vec{q} - \sum_i (\mu_i^L \dot{c}_i^L + \mu_i^T \dot{c}_i^T) + \vec{\nabla} \cdot \sum_i (\mu_i^L \vec{J}_i^L + \mu_i^T \vec{J}_i^T) + \pi \\ + T \left(\frac{\partial \underline{\sigma}}{\partial T} : \underline{\dot{\varepsilon}}^e + \frac{\partial \underline{X}}{\partial T} : \underline{\dot{\alpha}} + \frac{\partial R}{\partial T} \dot{r} - \frac{\partial Y}{\partial T} \dot{D} + \sum_i \frac{\partial \mu_i^L}{\partial T} \dot{c}_i^L + \sum_i \frac{\partial \mu_i^T}{\partial T} \dot{c}_i^T \right) \end{pmatrix}, \quad (28)$$

with $C_v = -T \frac{\partial^2 \psi}{\partial T^2}$ being the specific heat coefficient.

In order to take correctly into account all the multi-physical effects, the heat flux vector \vec{q} must now also depends not only on the gradient of temperature, but also on the chemical potential gradient of each specie by application of the thermodynamics of irreversible processes (Philibert, 1995):

$$\vec{q} = - \sum_m (L_{Tm}^L \vec{\nabla} \mu_m^L + L_{Tm}^T \vec{\nabla} \mu_m^T) - L_{TT}^T \vec{\nabla} T, \quad (29)$$

with $L_{Tm}^L, L_{Tm}^T, L_{TT}^T$ the so called kinetic coefficients of Onsager.

Equation (28) will be used to derive the weak variational functional associated with the thermal problem.

2.6 Diffusion Equations for Specie n

In this paragraph, we analyze now the diffusion of a given specie n , in order to see the evolution of its different concentrations (in lattice and in trapping sites) in the material with time.

Equations (10) and (11) give the expressions of chemical potentials for lattice and trapping sites respectively. The phenomenological model of volume diffusion is described in the present model not only as a function of the gradient of the chemical potentials, but also as a function of temperature (thermodiffusion) and pressure (barodiffusion) gradients. In the literature, the influence of these last gradients is often ignored because the simulations are of short duration. For the applications of our model, simulation time can be up to 100 years. In this case, it is then assumed that barodiffusion and thermodiffusion may have a significant influence. We define therefore for a given specie n (Philibert, 1995):

$$\vec{J}_n^L = - \sum_m L_{nm}^L \vec{\nabla} \mu_m^L - L_{np}^L \vec{\nabla} p - L_{nT}^L \vec{\nabla} T \quad \text{for lattice sites flux} \quad (30a)$$

$$\vec{J}_n^T = - \sum_m L_{nm}^T \vec{\nabla} \mu_m^T - L_{np}^T \vec{\nabla} p - L_{nT}^T \vec{\nabla} T \quad \text{for trapping sites flux,} \quad (31a)$$

with L_{nm}^i ($L_{nm}^i = L_{mn}^i$), L_{np}^i , L_{nT}^i , i ($= L, T$) the kinetic coefficients of Onsager.

These expressions assume that on one hand, there is a coupling between the species (i.e. the flux of the considered specie depends on the gradient of the chemical potential of the others species) and on the other hand that the gradient of interstitial chemical potential does not affect flux in trapping sites and reciprocally. The number of moles of lattice sites (N^L) is supposed to be constant, while that of trapping sites (N^T) is not constant. Replacing the gradient of chemical potentials in (30a) and (31a), we obtain:

$$\bar{J}_n^L = -\sum_m \left(D_{nm}^L \bar{\nabla} c_m^L + L_{nm}^L R \ln \left(\frac{\theta_m^L}{1-\theta_m^L} \right) \bar{\nabla} T - 3L_{nm}^L K\beta \sqrt{1-D} \bar{\nabla} (tr \underline{\underline{\varepsilon}}^e) \right) - L_{np}^L \bar{\nabla} p - L_{nT}^L \bar{\nabla} T \quad (30b)$$

And

$$\bar{J}_n^T = \begin{pmatrix} -\sum_m \left(D_{nm}^T \left[\bar{\nabla} c_m^T - \frac{c_m^T}{N^T} \bar{\nabla} N^T \right] + L_{nm}^T R \ln \left(\frac{\theta_m^T}{1-\theta_m^T} \right) \bar{\nabla} T - 3L_{nm}^T K\beta \sqrt{1-D} \bar{\nabla} (tr \underline{\underline{\varepsilon}}^e) \right) \\ -L_{np}^T \bar{\nabla} p - L_{nT}^T \bar{\nabla} T \end{pmatrix} \quad (31b)$$

With $D_{nm}^L = RT L_{nm}^L / c_m^L (1-\theta_m^L)$ and $D_{nm}^T = RT L_{nm}^T / c_m^T (1-\theta_m^T)$, the diffusion coefficients in lattice and trapping sites respectively. To explicit the expressions of these coefficients, we base our calculations on the formulation and hypotheses of Philibert (1995), and we obtain:

$$D_{nm}^L = \frac{D_{nm0}^L}{\Omega_m c_m^L (1-\theta_m^L)} \exp \left(-\frac{\Delta G}{RT} \right) \quad (32a)$$

$$D_{nm}^T = \frac{D_{nm0}^T}{\Omega_m c_m^T (1-\theta_m^T)} \exp \left(-\frac{\Delta G}{RT} \right) \quad (32b)$$

Diffusion coefficients are so functions of temperature, concentration, partial molar volume Ω_m and variation of the free energy of Gibbs ΔG .

The local balance equation for each specie n can be written in a single equation as the sum of the two mass balances (mass balance in lattice and in trapping sites):

$$\frac{dc_n^L}{dt} + \frac{dc_n^T}{dt} + \bar{\nabla} \cdot \bar{J}_n^L + \bar{\nabla} \cdot \bar{J}_n^T = 0 \quad (33)$$

Based on the classical and widely-used Oriani's postulate of "local equilibrium" between lattice and trapping ($\mu_n^L = \mu_n^T$), we model the concentration of trapping using, with $\theta_n^L \ll 1$:

$$c_n^T = \frac{N^T c_n^L K_n^T}{c_n^L K_n^T + N^L}, \quad (34)$$

with $K_n^T = \exp(\Delta\mu_n^b/RT)$, $\Delta\mu_n^b = \mu_{n0}^L - \mu_{n0}^T$ the trapping bending energy of specie n . According to other works (e.g. Krom et al., 1999), the number of moles of trapping sites depend on plastic strain ($N^T = N^T(\varepsilon^p)$). In our model, we consider that damage act as trap for species. Thus the number of moles of trapping sites is function not only of plastic strain but also of damage ($N^T = N^T(\varepsilon^p, D)$). With this definition and using equation (34), the evolution of c_n^T is then given by:

$$\frac{dc_n^T}{dt} = \frac{\partial c_n^T}{\partial c_n^L} \frac{dc_n^L}{dt} + \frac{\partial c_n^T}{\partial N^T} \left(\frac{\partial N^T}{\partial \varepsilon^p} \frac{d\varepsilon^p}{dt} + \frac{\partial N^T}{\partial D} \frac{dD}{dt} \right) + \frac{\partial c_n^T}{\partial K_n^T} \frac{dK_n^T}{dT} \frac{dT}{dt} \quad (35)$$

Replacing equation (35) in equation (33) and after some calculations, we obtain the evolution of c_n^L :

$$D^* \frac{dc_n^L}{dt} + \theta_n^T \left(\frac{\partial N^T}{\partial \varepsilon^p} \frac{d\varepsilon^p}{dt} + \frac{\partial N^T}{\partial D} \frac{dD}{dt} \right) - \frac{c_n^T (1 - \theta_n^T) \Delta \mu_n^b}{RT^2} \frac{dT}{dt} + \vec{\nabla} \cdot \vec{J}_n^L + \vec{\nabla} \cdot \vec{J}_n^T = 0, \quad (36)$$

with $D^* = 1 + c_n^T (1 - \theta_n^T) / c_n^L$.

Equations (34) and (36) will be used to analyze the diffusion of specie n in material.

2.7 Summary and Boundary Conditions

In this section, we summarize the equations to be solved in our isotropic thermo-mechanical-damage and diffusion coupled model, assuming the small strain hypothesis. In our model, we solve three equations:

Mechanical equation:

$$\text{div} \underline{\sigma} + \vec{f}_d = \rho \vec{\ddot{u}}, \quad (37)$$

where \vec{f}_d is the imposed body force vector and \vec{u} is the displacement vector.

Heat equation:

$$\rho C_v \dot{T} = \left(\underline{\sigma} : \underline{\dot{\varepsilon}}^p - \underline{X} : \underline{\dot{\alpha}} - R \dot{r} + Y \dot{D} - \vec{\nabla} \cdot \vec{q} - \sum_i (\mu_i^L \dot{c}_i^L + \mu_i^T \dot{c}_i^T) + \vec{\nabla} \cdot \sum_i (\mu_i^L \vec{J}_i^L + \mu_i^T \vec{J}_i^T) + \pi \right) + T \left(\frac{\partial \underline{\sigma}}{\partial T} : \underline{\dot{\varepsilon}}^e + \frac{\partial \underline{X}}{\partial T} : \underline{\dot{\alpha}} + \frac{\partial R}{\partial T} \dot{r} - \frac{\partial Y}{\partial T} \dot{D} + \sum_i \frac{\partial \mu_i^L}{\partial T} \dot{c}_i^L + \sum_i \frac{\partial \mu_i^T}{\partial T} \dot{c}_i^T \right) \quad (28)$$

Specie diffusion equation:

$$D^* \frac{dc_n^L}{dt} + \theta_n^T \left(\frac{\partial N^T}{\partial \varepsilon^p} \frac{d\varepsilon^p}{dt} + \frac{\partial N^T}{\partial D} \frac{dD}{dt} \right) - \frac{c_n^T (1 - \theta_n^T) E_n^b}{RT^2} \frac{dT}{dt} + \vec{\nabla} \cdot \vec{J}_n^L + \vec{\nabla} \cdot \vec{J}_n^T = 0 \quad (36)$$

Boundary conditions. We add to the three previous equations the usual boundary conditions (Dirichlet and Neumann) to complete the theory. Let V be the volume of the body and S the boundary of the body.

Mechanical boundary conditions: the boundaries S_u , S_F and S_c are parts of boundary S where the displacement \vec{u} , the traction forces \vec{t} and the contact forces \vec{t}_c are prescribed: $\vec{u} = \vec{u}_s$ on S_u , $\underline{\sigma} \cdot \vec{n} = \vec{t}$ on S_F and $\underline{\sigma} \cdot \vec{n} = \vec{t}_c$ on S_c ; with $S = S_u \cup S_F \cup S_c$ and $S_u \cap S_F \cap S_c = \emptyset$.

Thermal boundary conditions: S_T is the part of the boundary S where the temperature T is imposed and S_q is the boundary where the heat flux vector \vec{q} is prescribed: $T = T_s$ on S_T and $\vec{q} = \vec{q}$ on S_q ; with $S = S_T \cup S_q$ and $S_T \cap S_q = \emptyset$.

Diffusion boundary conditions: S_{cL} is the part of the boundary S where lattice concentration of specie n is imposed and S_{JL} the part of the boundary S where diffusion flux in lattice sites of specie n is prescribed: $c_n^L = c_n^{Le}$ on S_{cL} and $\vec{J}_n^L \cdot \vec{n} = \vec{J}_n$ on S_{JL} ; with $S = S_{cL} \cup S_{JL}$ and $S_{cL} \cap S_{JL} = \emptyset$. Only lattice concentration is our variable, therefore we don't need boundary conditions for trapping.

Considering the equilibrium between the dissolved specie n and its gas, which leads to equality between the different chemical potentials, we obtain the c_n^{Le} value to be applied for Dirichlet boundary condition. This is different from Di Leo and Anand (2013) that have used in their model the lattice chemical potential as variable. So, these authors have preferentially used the lattice chemical potential as the imposed boundary condition. However, we consider in the present problem that it is physically more consistent to use concentration as variable.

3 Non-coupled Model: Hydrogen Diffusion in TA6V

In this section, we present only diffusion model for hydrogen diffusion in TA6V metal. This is therefore a totally uncoupled model for diffusion. In this case, equation (36) becomes simply:

$$D^* \frac{dc_H^L}{dt} + \vec{\nabla} \cdot \vec{J}_H^L + \vec{\nabla} \cdot \vec{J}_H^T = 0 \quad (36bis)$$

We have implemented equation (36bis) in the finite element software Abaqus/Standard, 2013, by writing a user element (Uel) with four isoparametric nodes (see Diamantopoulou et al. 2017). It is used to test hydrogen diffusion in TA6V metal after welding. The welding used two plates, each 50 mm long and 30 mm wide. After welding, a metal has 60 mm long and 50 mm wide, and has three zones: fused zone (FZ), heat affected zones (HAZ) and base metal (BM) who was not affected by welding. The schematic geometry and the mesh used are given on Figure 1. FZ length is taken to 7 mm and each HAZ length to 1 mm. The meshes are more refined in FZ, HAZ and near HAZ than for BM in order to describe all the phenomena occurring in the affected zones. The mesh element size is 1 mm x 1 mm for the FZ, 0.5 mm x 1 mm for the HAZ. For the BM, the mesh element size increases from 1 mm x 1 mm to 1.5 mm x 1 mm from the HAZ.

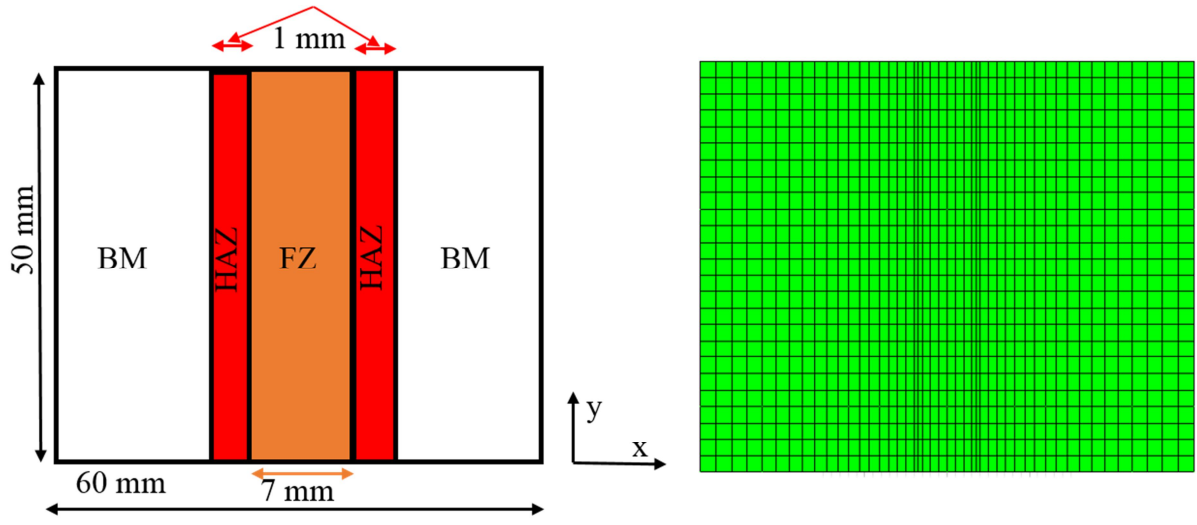


Figure 1. Schematic geometry (left) and mesh (right)

We consider initial zero concentration of hydrogen for all the zones and constant diffusion coefficients. For boundary conditions, only Dirichlet conditions are used. c_H^{Le} is calculated from equilibrium ($2\mu_H^L = \mu_{H_2}^L$) by

$$c_H^{Le} = \frac{N^L}{\sqrt{p^0}} \exp\left(\frac{-\mu_{H_2}^L}{RT}\right) \sqrt{p_{H_2}},$$

which is imposed on the left side of metal, with p^0 the reference pressure,

p_{H_2} the dihydrogen pressure. At the right side of the metal, we impose zero concentration. Table 1 gives the different numerical values of the parameters. For BM, only trapping coefficient of diffusion value comes from Díaz et al. (2016); the others values come from Di Leo and Anand (2013). Some values are slightly modified for HAZ and FZ. The temperature is taken to 298K for all zones. According to Krom et al. (1999), the number of moles of trapping sites N^T is assumed to increase with an increase in equivalent plastic strain ε^p according to this expression: $\log N^T = 23.26 - 2.33 \exp(-5.5\varepsilon^p)$. In the present case without plastic strain, we use $\log N^T = 20.93$.

Table 1 Diffusion properties

Variables	BM	HAZ	FZ
D_0^L (m ² /s)	1.27×10^{-8}	1.43×10^{-8}	1.59×10^{-8}
D_0^T (m ² /s)	4.53×10^{-18}	4.70×10^{-18}	5.22×10^{-18}
N^L (mol/m ³)	8.47×10^5	8.47×10^5	8.47×10^5
$\Delta\mu_n^b$ (J/mol)	-60×10^3	-60×10^3	-60×10^3
$\mu_{H_2}^L$ (J/mol)	28.6×10^3	28.6×10^3	28.6×10^3

To validate the Uel subroutine, we use both Uel subroutine and the existing diffusion element of Abaqus named DC2D4 (which does not take into account the presence of traps) with the same diffusion properties (normal diffusion only) to simulate diffusion problem. Figure 2 shows the comparison of the distribution of normalized lattice hydrogen concentration (c_H^L/c_H^{Le}) obtained with Uel and with Abaqus at $t = 0.5$ and $t = 1$ year. So we can say with respect to the Figure 2 that the Uel subroutine is well implemented and thus valid this first stage of our model.

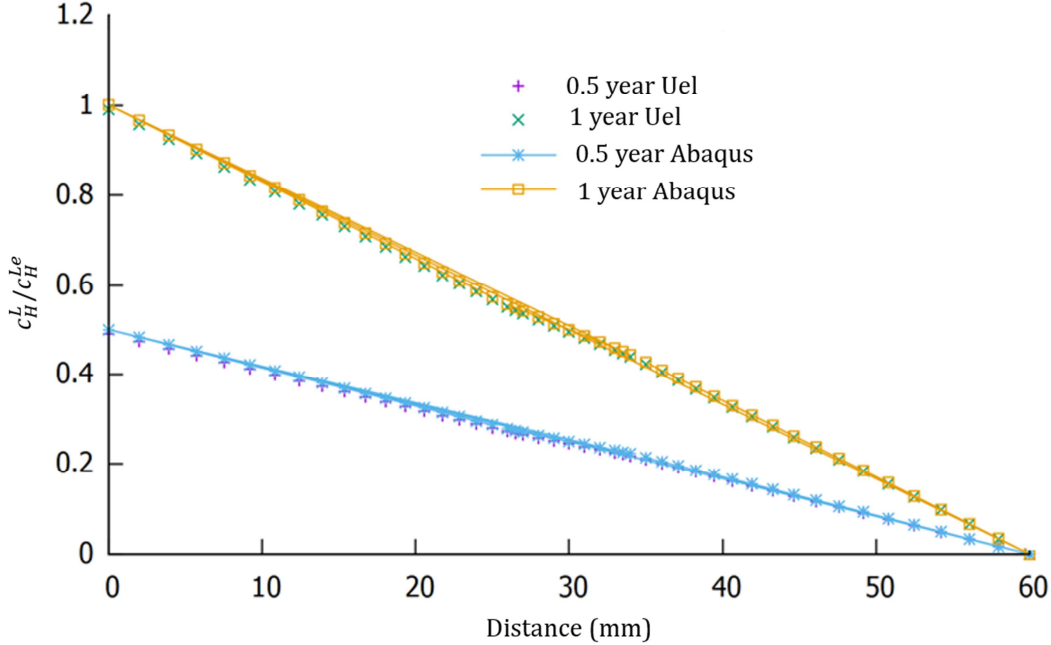


Figure 2. Comparison Uel-Abaqus of normalized lattice hydrogen concentration at $t = 0.5$ year and $t = 1$ year

Figure 3 shows the distribution of normalized lattice hydrogen concentration (c_H^L/c_H^{Le}) to the left, and normalized trapping hydrogen concentration (c_H^T/c_H^{Te}) to the right in the metal for different simulation times. Increase in the different normalized hydrogen concentrations is observed, which reflects hydrogen diffusion in metal. The increase of trapping hydrogen concentration is more than the increase in lattice hydrogen concentration. The same observations are made in existing models (e.g. Di Leo and Anand, 2013; Díaz et al., 2016).

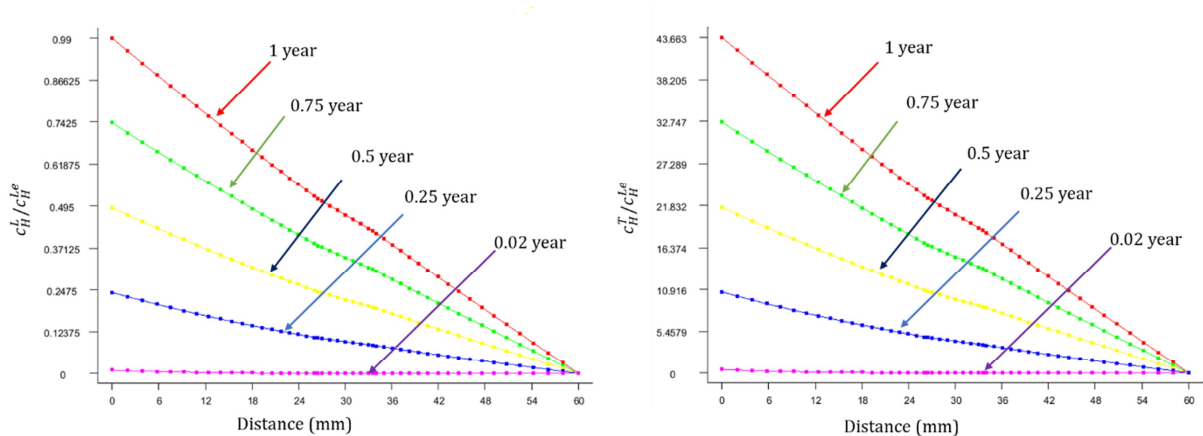


Figure 3. Normalized lattice hydrogen concentration c_H^L/c_H^{Le} (left) and normalized trapping hydrogen concentration c_H^T/c_H^{Te} (right) with time.

To check if the diffusion in trapping sites has an effect on our results, we perform a second simulation taking $D_H^T = 0 \Rightarrow \vec{J}_H^T = 0$ for all zones. Figure 4 shows the comparison between c_H^L/c_H^{Le} with \vec{J}_H^T and without \vec{J}_H^T to the left, and c_H^T/c_H^{Te} with \vec{J}_H^T and without \vec{J}_H^T to the right. The comparison shows that at this stage of our simulations, \vec{J}_H^T has no influence on our results.

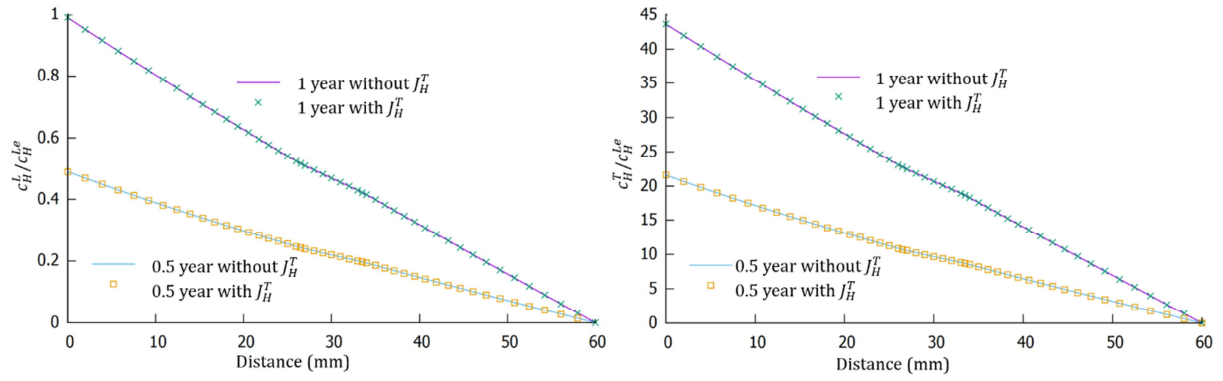


Figure 4. Normalized lattice hydrogen concentration c_H^L/c_H^{Le} (left) and normalized trapping hydrogen concentration c_H^T/c_H^{Le} (right) with and without J_H^T for $t = 0.5$ year and $t = 1$ year.

4 Conclusion and Perspectives

A fully coupled thermo-elasto-visco-plastic and diffusion model has been presented from a theoretical point of view. This model includes the different hardenings (isotropic and kinematic) in the material, ductile damage and is based on the thermodynamics of irreversible processes with state variables and assuming the small strain hypothesis. This is the first time that a coupled theory for species diffusion and thermo-elasto-visco-plastic model takes into account ductile damage and both kinematic and isotropic hardenings. The different concentrations are introduced as internal variables, which allowed us obtaining chemical potentials as a derivative of state potential (taken equal to the Helmholtz specific free energy). Diffusion contribution is taken into account through internal energy balance and entropy balance. Therefore a generalized Clausius-Duhem dissipation inequality is proposed.

The uncoupled model for hydrogen diffusion showed the increase in both lattice and trapping hydrogen concentrations. But the increase in trapping hydrogen concentration is more important than the increase in lattice hydrogen concentration. The first study on the influence of trapping diffusion coefficient (trapping flux) has shown that, at this stage, this coefficient does not influence significantly the numerical results.

In future prospects, we will validate the fully coupled model with only hydrogen as diffusing specie and with hydrogen and oxygen as diffusing species. After validation of the model, numerical simulations will be made as well as studies of sensibility for some parameters of the model.

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Address: Department of Engineering Mechanics and Mechanics of Materials, ICD/LASMIS, CNRS UMR 6281. University of Technology of Troyes, CS 42060, 10004 Troyes Cedex, France
email: kanssounesaliya@utt.fr, benoit.panicaud@utt.fr, carl.labergere@utt.fr