SOLID MECHANICS RESEARCH OFFICE

Dr. A.G. VARIAS

fax/tel.: +30 - (0)1 - 2849916
e-mail : varias@hol.gr

Makedonias 17
N. Iraklio 141 21
Athens
Greece

Mathematical Model for Hydrogen Diffusion, Energy Flow and Hydride Formation in Zirconium under Stress

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Abstract

Hydrogen embrittlement contributes to the degradation of zirconium alloy fuel cladding in light water reactors. The mechanism includes several coupled processes: (i) hydrogen diffusion, (ii) non-mechanical energy flow, (iii) hydride formation and (iv) hydride/solid solution deformation.

Simulation of damage growth requires the consideration of all the above processes as well as of hydride fracture.

In this report, a mathematical model is presented for hydrogen embrittlement. The model includes the governing differential equations for hydrogen diffusion and non-mechanical energy flow, the constitutive relation for zirconium deformation and an expression for hydrogen terminal solid solubility. Coupling of all four processes is taken into account. Both hydrogen diffusion and energy flow depend on hydrogen chemical potential and temperature gradients. Consequently they depend on stress gradient due to the stress-dependence of the chemical potential. Hydride precipitation occurs, when hydrogen concentration exceeds the terminal solid solubility of hydrogen in zirconium, which depends on temperature, applied stress and, because of hydride expansion during formation, on the works of hydride accommodation and interaction with the applied stress field. Finally material deformation depends on hydrogen diffusion, energy flow and hydride precipitation due to thermal, hydrogen-dissolution induced and hydride-formation induced expansion.

The present work is part of a study, which also includes a de-cohesion model for hydride fracture and a finite element implementation of the governing equations for all processes.

List of Symbols

a	zirconium thermal expansion coefficient,
C^H (or C^{Hy})	solid solution hydrogen concentration per unit volume of solid solution (or per unit volume of hydride/solid-solution material),
$C^{H,hr}$	hydride hydrogen concentration per unit volume of hydride,
C^{HT}	total hydrogen concentration per unit volume,
C^{TS} ($C^{TS,0}$)	hydrogen terminal solid solubility in zirconium (under stress free conditions),
C^{hr}	hydride concentration per unit volume of hydride/solid-solution material,
C^{Zr}	zirconium concentration per unit volume of hydride/solid-solution material,
c_p (c_σ)	specific heat of zirconium at constant pressure (constant stress),
D^H	hydrogen diffusion coefficient in zirconium,
E	zirconium elasticity modulus,
f	hydride volume fraction,
J_i^E ($J_i^{E,SS}$)	non-mechanical energy flux (in solid solution),
J_i^H ($J_i^{H,SS}$)	hydrogen flux (in solid solution),
k	thermal conductivity of zirconium,
L^E, L^H, L^{EH}, L^{HE}	coefficients of thermodynamic equations of motion,
M_{ijkl}	elastic compliance tensor of zirconium,
N^B	number of moles of component B,
N^H	number of moles of hydrogen,
N^{hr}	number of moles of hydride,
N^{Zr}	number of moles of zirconium,
n_k	unit vector normal to surface S, pointing outwards,
Q^H	hydrogen heat of transport in zirconium,
R	gas constant,
S	surface of volume V,
S	entropy per unit volume,
S_i	entropy flux,
s	specific entropy,
T	temperature (^{o}K),
t	time,
u	specific internal energy,
V	volume,
$\overline{V}$	solid solution molal volume,
$\overline{V}^H$	hydrogen molal volume,
$\overline{V}^{hr}$	hydride molal volume,
$\overline{V}^{Zr}$	zirconium molal volume,

v_i	thermodynamic substate variables,
W^B	work performed per mole of addition of component B,
W^H	work performed per mole of addition of hydrogen,
W^{hr}	work performed per mole of addition of hydride,
W^{Zr}	work performed per mole of addition of zirconium,
w	strain energy,
$\overline{w}_{acc}$	strain energy of accommodation per mole of hydride,
$\overline{w}_{int}$	interaction strain energy per mole of hydride,
$\overline{w}_{af}$	strain energy of externally applied field per mole of hydride,
X_i^E	thermodynamic force for non-mechanical energy flow,
X_i^H	thermodynamic force for hydrogen diffusion,
x	hydrogen moles per hydride mole (ZrH_x),
x_i	Cartesian co-ordinates,
$\Delta\overline{H}^{hr}$	molal enthalpy of hydride formation,
δ_{ij}	Kronecker delta,
ε_{ij}	strain tensor,
ε_{ij}^E	thermal expansion strains,
ε_{ij}^H	strains caused by hydrogen dissolution and hydride precipitation,
ε_{ij}^T	hydride transformation strains,
θ	rate of internal generation of entropy per unit volume,
θ^H	zirconium lattice expansion, when a mole of hydrogen dissolves in a mole of zirconium,
θ^{hr}	hydride volume expansion,
λ, μ	zirconium Lame constants,
μ^B ($\mu^{B,0}$)	chemical potential of component B (under stress-free conditions),
μ^H ($\mu^{H,0}$)	hydrogen chemical potential (under stress-free conditions),
$\mu^{H,RS}$	stress-free hydrogen chemical potential in the reference state,
μ^{hr} ($\mu^{hr,0}$)	hydride chemical potential (under stress-free conditions),
μ^{Zr} ($\mu^{Zr,0}$)	zirconium chemical potential (under stress-free conditions),
ρ	mass density,
σ_n	stress normal to the hydride/solid-solution interface,
σ_{ij}	stress tensor,
σ_{ij}^I	hydride stresses, caused by hydride transformation,
τ_i	thermodynamic tensions,
χ^H	hydrogen mole fraction in solid solution.

1. Introduction

Zirconium alloy in fuel cladding of light water reactors is under temperature gradient, during reactor operation. Also the generation of micro-cracks on the external corroded surface introduces significant stress gradients. Consequently the degradation of the material due to hydrogen, generated by oxidation on the external cladding surface, is affected by several interrelated processes, namely: (i) hydrogen diffusion, (ii) non-mechanical energy flow, (iii) hydride formation and (iv) hydride/solid solution deformation.

The importance of temperature gradient on hydrogen redistribution and hydride formation has been discussed in previous studies. In the early works by Sawatzky (1960), Sawatzky and Vogt (1963) and Marino (1972) solutions for hydrogen diffusion and hydride precipitation under time-independent temperature distributions were presented. Also in a recent work by Forsberg and Massih (1990) the redistribution of hydrogen in fuel cladding was presented under conditions, for hydrogen pick-up and temperature distribution, encountered in practice.

The objective of this report is to build on the previous studies and present a mathematical model, which takes into account the existing coupling of all processes leading to zirconium degradation, due to hydrogen embrittlement. This model, together with a de-cohesion approach for hydride fracture, will be used in order to estimate damage growth in nuclear fuel cladding.

The structure of the report is as follows. In section 2, the thermodynamic equations of motion, which relate hydrogen and non-mechanical energy flux with temperature and chemical potential gradients, are presented. The derivations, based on continuum thermodynamics as well as on the thermodynamics of irreversible processes, have been specialized for the material under consideration, which is made of zirconium/hydrogen solid solution and hydrides. In sections 3 and 4 the governing equations for hydrogen diffusion and energy flow, respectively, are derived. The term energy flow is used instead of heat conduction, because the analysis includes also the energy transported by hydrogen atoms. In section 5 hydrogen chemical potential and its terminal solid solubility in zirconium under stress is presented. The dependence of the chemical potential on stress leads to an effect of stress gradient on hydrogen diffusion and energy flow. In section 6 the constitutive relations for the deformation of zirconium are presented. The effect of lattice expansion due to hydrogen dissolution, hydride formation and thermal strains is included. Finally conclusion are given in section 7.

In the following, low case Latin indices are used to denote components of tensors of various orders; repeated indices in a term of an expression denote summation. Also the superscripts B, H (or Hy), E, SS, Zr, hr are used to relate a quantity to component B, hydrogen, non-mechanical energy, solid solution, zirconium and hydride respectively; repetition of B, H, E, SS, Zr, hr in an equation does not imply summation. In addition, the superscript RS is used to denote the stress-free chemical potential for a reference state.

2. Thermodynamic Equations of Motion

Energy flow and diffusion of mass are generally coupled processes. A temperature gradient leads to flow of matter and therefore to a concentration gradient. Conversely a diffusion process gives rise to a temperature difference. A detailed discussion and relevant references for the thermodynamic treatment of energy-flow/diffusion as well as of other coupled phenomena are presented by Denbigh (1951). His treatise for irreversible processes is based on Onsager's principle of microscopic reversibility. In the following, the theory is applied to the processes of hydrogen diffusion and energy flow, occurring within zirconium fuel cladding.

According to the empirical law of Fourier, heat flux is linearly related to the temperature gradient, which is the thermodynamic force, driving heat flow. In the case of diffusion the classical Fick's law has been modified; in an isothermal system, the flux of a diffusing substance is proportional to the gradient of its chemical potential. Then, chemical potential is the thermodynamic force driving diffusion under isothermal conditions. When the processes operate simultaneously, as in the case of hydrogen diffusion and energy flow in the fuel cladding, the coupling is taken into account by assuming that the non-mechanical energy and hydrogen fluxes are linearly related to both thermodynamic forces:

$$J_i^E = L^E X_i^E + L^{EH} X_i^H \; , \tag{2.1a}$$

$$J_i^H = L^{HE} X_i^E + L^H X_i^H \; , \tag{2.1b}$$

$$L^{EH} = L^{HE} \; , \tag{2.1c}$$

where J_i^E and J_i^H are the non-mechanical energy flux and the hydrogen flux, respectively. It noted that the energy flux includes pure heat flow, which is described by Fourier law, and the energy transported by the diffusing hydrogen. X_i^E and X_i^H are the thermodynamic forces driving energy flow and hydrogen diffusion, respectively. Relation (2.1c) is valid due to Onsager reciprocity relation. Relations (2.1a,b) are the thermodynamic equations of motion for the coupled energy flow and hydrogen diffusion.

The thermodynamic forces are related to the gradients of temperature and hydrogen chemical potential. Their definition satisfies the following relation for the rate of internal generation of entropy per unit volume, θ, caused by hydrogen diffusion and energy flow:

$$\mathrm{T}\theta = J_i^E X_i^E + J_i^H X_i^H \; . \tag{2.2}$$

In the following the derivation of the thermodynamic forces is presented.

Continuum thermodynamics, based on a caloric equation of state, assumes that the local internal energy per unit mass, u, is determined by the thermodynamic state, specified by n thermodynamic substate variables, $v_1, v_2, ..., v_n$, and the specific entropy, s (e.g. Truesdell and Toupin, 1960). The substate variables could be strains and concentrations of substances. In the present study, the material under consideration is made of hydrogen/zirconium solid solution and zirconium hydride, ZrH_x. Then, the

strains, ε_{ij}, and the concentrations of hydrogen and zirconium, being in solid solution, as well as of hydride, C^{Hy}, C^{Zr}, C^{hr}, respectively, can be chosen as substate variables. Note that the above three local concentrations are defined with respect to the volume, which is occupied by all phases.

The variation of specific internal energy for a material particle is given by the relation:

$$du = \mathrm{T}ds + \tau_i dv_i.$$ (2.3)

The thermodynamic tensions, τ_i, for the strains and the concentrations of the various components are related to the actual stresses and the chemical potentials of the components, respectively. When the mechanical work is fully recoverable, as in the present study, which is based on elastic material deformation, and there are no kinematical or thermodynamic constraints, the mechanical power for a material particle equals to the internal energy rate due to the thermodynamic tensions, associated with the strains. Then, for a particle of the material under consideration, the internal energy variation is:

$$\rho du = \rho \mathrm{T}ds + \sigma_{ij}d\varepsilon_{ij} + \mu^H dC^{Hy} + \mu^{Zr} dC^{Zr} + \mu^{hr} dC^{hr}.$$ (2.4)

The concentrations are given in moles per unit volume.

Hydride precipitation is assumed to occur under equilibrium conditions:

$$\mu^{hr} = \mu^{Zr} + \mathrm{x}\mu^H.$$ (2.5)

The total mass of Zirconium in solid solution and in hydride is constant. Consequently, $dC^{Zr} = -dC^{hr}$, which leads to the following simplification:

$$\mu^H dC^{Hy} + \mu^{Zr} dC^{Zr} + \mu^{hr} dC^{hr} =$$

$$\mu^H \left(dC^{Hy} + \mathrm{x}dC^{hr}\right) + \left(\mu^{hr} - \mu^{Zr} - \mathrm{x}\mu^H\right)dC^{hr} = \mu^H dC^{HT},$$ (2.6)

where C^{HT} is the total hydrogen concentration in solid solution and hydride. By replacing (2.6) into (2.4), one may derive the rate of internal energy for a particle of the material:

$$\rho \frac{du}{dt} = \rho \mathrm{T}\frac{ds}{dt} + \sigma_{ij}\frac{d\varepsilon_{ij}}{dt} + \mu^H \frac{dC^{HT}}{dt}.$$ (2.7)

The conservation of energy, which requires that the internal energy rate equals the energy input rate due to the external stress power and the non-mechanical energy flow, is expressed by the following well known relation (e.g. Malvern,1969):

$$\rho \frac{du}{dt} = \sigma_{ij}\frac{d\varepsilon_{ij}}{dt} - \frac{\partial J_k^E}{\partial x_k}.$$ (2.8)

The minus sign is due to the convention that the energy flux is positive when it leaves the body. Note that the non-mechanical energy flux in (2.8) is identical to that defined in (2.1) and therefore includes pure heat flow as well as energy transported by hydrogen.

According to the mass balance for hydrogen, described in Section 3:

$$\frac{dC^{HT}}{dt} = -\frac{\partial J_k^H}{\partial x_k} . \tag{2.9}$$

Substitution of (2.8) and (2.9) into (2.7), leads to the following expression, after some algebraic manipulations:

$$\rho \frac{ds}{dt} + \frac{\partial}{\partial x_k}\left(\frac{J_k^E - \mu^H J_k^H}{\text{T}} \right) = -\frac{J_m^E}{\text{T}^2}\frac{\partial \text{T}}{\partial x_m} - J_n^H \frac{\partial}{\partial x_n}\left(\frac{\mu^H}{\text{T}} \right) . \tag{2.10}$$

Let us define:

$$\theta = -\frac{J_k^E}{\text{T}^2}\frac{\partial \text{T}}{\partial x_k} - J_m^H \frac{\partial}{\partial x_m}\left(\frac{\mu^H}{\text{T}} \right) , \tag{2.11a}$$

$$S_k = \frac{J_k^E - \mu^H J_k^H}{\text{T}} , \tag{2.11b}$$

integrate over a volume V and apply Gauss's divergence theorem. Then (2.10) leads to the following relation on entropy variation over a volume V:

$$\frac{d}{dt}\int_V \rho s\, dV + \int_S S_k n_k\, dS = \int_V \theta\, dV , \tag{2.12}$$

where S is the boundary of the volume V and n_k the normal vector, pointing outwards. The first term of the left-hand side provides the rate of entropy in the specified volume. The second term of the left-hand side represents the rate of outflow of entropy, or in other words the rate of entropy due to heat and hydrogen flux on the bounding surface. Consequently the term of the right-hand side is the rate of internal generation of entropy. Therefore θ, defined in (2.11a), is the rate of generation of entropy per unit volume and satisfies relation (2.2). The thermodynamic forces for energy flow and hydrogen diffusion are then defined as follows:

$$X_i^E = -\frac{1}{\text{T}}\frac{\partial \text{T}}{\partial x_i} , \tag{2.13a}$$

$$X_i^H = -\text{T}\frac{\partial}{\partial x_i}\left(\frac{\mu^H}{\text{T}} \right) . \tag{2.13b}$$

More details on the thermodynamic equations of motion, taking into account all the features of the problem under consideration, are presented in the following sections 3 and 4.

3. Hydrogen Diffusion

When hydrogen and zirconium form a solid solution, under temperature and chemical potential gradients, the hydrogen flux has been found to satisfy the following relation (e.g. Shewmon, 1963):

$$J_k^{H,SS} = -\frac{D^H C^H}{R\text{T}}\left(\frac{\partial \mu^H}{\partial x_k} + \frac{Q^H}{T}\frac{\partial \text{T}}{\partial x_k}\right), \tag{3.1}$$

where R is the gas constant. Also C^H, D^H and Q^H are the concentration, the diffusion coefficient and the heat of transport of hydrogen in zirconium, respectively. Experimental values for D^H and Q^H can be found in literature (e.g. Kammenzind et al., 1996; Kearns, 1972).

Hydrogen diffusion in the hydride is relatively very slow and it could be described by a relation similar to (3.1). However there are significant discrepancies in the values for the diffusion coefficient and the heat of transport of hydrogen in the hydride, proposed by various scientists (Maki and Sato, 1975); these values are therefore not reliable. Also according to Marino (1972), no significant improvement of the predictions of the diffusion models is expected by considering hydrogen diffusion in the hydride. For these reasons hydrogen diffusion in the hydride is neglected in the present study. Then, if f is the volume fraction of the hydride in the material, the total hydrogen flux is given by the following relation:

$$J_k^H = -(1-f)\frac{D^H C^H}{R\text{T}}\left(\frac{\partial \mu^H}{\partial x_k} + \frac{Q^H}{T}\frac{\partial \text{T}}{\partial x_k}\right). \tag{3.2}$$

Mass conservation requires that the rate of total hydrogen concentration, C^{HT}, inside a volume V, is equal to the rate of hydrogen moles flowing through the boundary S:

$$\frac{d}{dt}\int_V C^{HT} dV + \int_S J_k^H n_k dS = 0. \tag{3.3}$$

Relation (3.3) is valid for an arbitrary volume. Then, one may derive the respective differential equation, by using divergence theorem:

$$\frac{dC^{HT}}{dt} = -\frac{\partial J_k^H}{\partial x_k}. \tag{3.4}$$

Note that the total hydrogen concentration, C^{HT}, is related to the solid solution, C^H, and the hydride, $C^{H,hr}$, concentrations of hydrogen as follows:

$$C^{HT} = f C^{H,hr} + (1 - f) C^{H} .$$ (3.5)

C^{H} is defined with respect to the volume occupied by solid solution, i.e. $(1-f)V$; consequently C^{Hy}, defined in the previous section, equals to $(1 - f) C^{H}$. C^{H} is equal to the hydrogen terminal solid solubility, C^{TS}, when $f \neq 0$. Similarly $C^{H,hr}$ is defined with respect to the volume occupied by the hydride, i.e. fV, and therefore it can be considered constant, independent of temperature.

4. Energy Flow

The derivation of the equations, which describe flow of energy, is based on the relations of sections 2 and 3. Initially, hydrogen/zirconium solid solution is considered. Comparison of relations (3.1), (2.1b,c) and (2.13a,b) leads to the determination of the following coefficients of the thermodynamic equations of motion:

$$L^{H} = \frac{D^{H} C^{H}}{R \mathrm{T}} ,$$ (4.1a)

$$L^{HE} = L^{EH} = \frac{D^{H} C^{H}}{R \mathrm{T}} \left(Q^{H} + \mu^{H} \right).$$ (4.1b)

The remaining coefficient L^{E} can be determined, by taking into account the well known empirical law of Fourier for heat conduction:

$$J_{i}^{E} = -k \frac{\partial \mathrm{T}}{\partial x_{i}} .$$ (4.2)

k is the thermal conductivity of zirconium. Note that relation (4.2) is valid, when there is no hydrogen diffusion:

$$J_{i}^{H,SS} = 0 \overset{(3.1)}{\Rightarrow} \frac{\partial \mu^{H}}{\partial x_{i}} = -\frac{Q^{H}}{\mathrm{T}} \frac{\partial \mathrm{T}}{\partial x_{i}} .$$ (4.3)

By substituting (4.3) and (2.13a,b) into (2.1a), one may derive:

$$J_{i}^{E} = -\left[L^{E} - L^{EH} \left(Q^{H} + \mu^{H} \right) \right] \frac{1}{\mathrm{T}} \frac{\partial \mathrm{T}}{\partial x_{i}} \overset{(4.2)}{=} -k \frac{\partial \mathrm{T}}{\partial x_{i}} \overset{(4.1b)}{\Rightarrow}$$

$$L^{E} = k \mathrm{T} + \frac{D^{H} C^{H}}{R \mathrm{T}} \left(Q^{H} + \mu^{H} \right)^{2} .$$ (4.4)

Having determined all the coefficients of the thermodynamic equations of motion, the expression for energy flux in hydrogen/zirconium solid solution takes the following form:

$$J_i^{E,SS} = \left(Q^H + \mu^H\right)J_i^{H,SS} - k\frac{\partial T}{\partial x_i} \ . \tag{4.5}$$

Note that the energy flux includes the two contributions, mentioned earlier, i.e. the energy transported by hydrogen atoms, which is the first term of the right-hand side, and the conducted heat. Also note that hydrogen heat of transport is the energy transported by hydrogen in excess of its chemical potential and therefore, according to relations (2.10)-(2.12), contributes to the variation of entropy.

According to the discussion in section 3, the energy flow in the hydride is only due to heat conduction. It is assumed that the thermal conductivity of the hydride equals the thermal conductivity of zirconium. Then, the following relation provides the total energy flux in a solid solution / hydride material:

$$J_i^E = (1-f)J_i^{E,SS} - fk\frac{\partial T}{\partial x_i} \overset{(3.1),(3.2),(4.5)}{\Rightarrow}$$

$$J_i^E = \left(Q^H + \mu^H\right)J_i^H - k\frac{\partial T}{\partial x_i} \ . \tag{4.6}$$

In order to completely describe the process of energy flow, the conservation of energy should be taken into account. Combination of relations (2.7)-(2.9) leads to the following differential equation of energy balance:

$$\rho T\frac{ds}{dt} = \mu^H\frac{\partial J_i^H}{\partial x_i} - \frac{\partial J_m^E}{\partial x_m} \overset{(4.6)}{\Rightarrow}$$

$$\rho T\frac{ds}{dt} = \frac{\partial}{\partial x_i}\left(k\frac{\partial T}{\partial x_i}\right) - Q^H\frac{\partial J_m^H}{\partial x_m} - J_n^H\frac{\partial \mu^H}{\partial x_n} \ . \tag{4.7}$$

The entropy rate is derived by taking into account its dependence on all thermodynamic variables (i.e. temperature, stress as well as hydride, zirconium and hydrogen concentrations):

$$\frac{dS}{dt} = \frac{\partial S}{\partial T}\frac{dT}{dt} + \frac{\partial S}{\partial \sigma_{ij}}\frac{d\sigma_{ij}}{dt} +$$

$$+ \frac{\partial S}{\partial C^{hr}}\frac{dC^{hr}}{dt} + \frac{\partial S}{\partial C^{Zr}}\frac{dC^{Zr}}{dt} + \frac{\partial S}{\partial C^{Hy}}\frac{dC^{Hy}}{dt} =$$

$$= \frac{\partial S}{\partial T}\frac{dT}{dt} + \frac{\partial S}{\partial \sigma_{ij}}\frac{d\sigma_{ij}}{dt} +$$

$$+ \left(\frac{\partial S}{\partial C^{hr}} - \frac{\partial S}{\partial C^{Zr}} - x\frac{\partial S}{\partial C^{Hy}}\right)\frac{dC^{hr}}{dt} + \frac{\partial S}{\partial C^{Hy}}\frac{dC^{HT}}{dt} \ .$$

S is the entropy per unit volume. Note that entropy partial derivative with respect to temperature is related to the specific heat of solid solution / hydride material under constant stress, $c_\sigma = \mathrm{T}(\partial s/\partial \mathrm{T})_\sigma$, which is taken equal to the specific heat of zirconium at constant pressure, c_p. Elastic deformation does not produce entropy and consequently the partial derivative of entropy with respect to stress is zero. The term in parenthesis represents the entropy production due to hydride formation; therefore it is equal to $\Delta \overline{H}^{hr}/\mathrm{T}$, where $\Delta \overline{H}^{hr}$ is the enthalpy associated with the formation of a mole of hydride. Also, $\partial S/\partial C^{Hy}$ represents the change of entropy due to the addition of a mole of hydrogen in the solid solution, which is equal to Q^H/T. Finally, dC^{HT}/dt is related to hydrogen flux (relation (3.4)) and $dC^{hr}/dt = (1/\overline{V}^{hr})df/dt$. Consequently entropy rate is given by the following relation:

$$\rho \mathrm{T} \frac{ds}{dt} = \rho c_p \frac{d\mathrm{T}}{dt} + \frac{\Delta \overline{H}^{hr}}{\overline{V}^{hr}} \frac{df}{dt} - Q^H \frac{\partial J_k^H}{\partial x_k} . \tag{4.8}$$

Substitution of (4.8) into (4.7) leads to the following differential equation which governs the flow of non-mechanical energy:

$$\rho c_p \frac{d\mathrm{T}}{dt} + \frac{\Delta \overline{H}^{hr}}{\overline{V}^{hr}} \frac{df}{dt} = \frac{\partial}{\partial x_i}\left(k \frac{\partial \mathrm{T}}{\partial x_i} \right) - J_n^H \frac{\partial \mu^H}{\partial x_n} . \tag{4.9}$$

5. Hydrogen Chemical Potential and Terminal Solid Solubility in Zirconium under Stress

According to the mathematical formulation for hydrogen diffusion and energy flow, discussed in previous sections, the knowledge of hydrogen chemical potential and terminal solid solubility is necessary. Both these quantities depend on the stress, which is applied on zirconium. The relations for theses quantities are derived in the following.

The chemical potentials of mobile and immobile components in stressed solids have been derived by Li et al. (1966). According to their study, the chemical potential of a component B is given by the following relation:

$$\mu^B = \mu^{B,0} + \frac{\partial w}{\partial N^B} - W^B . \tag{5.1}$$

$\mu^{B,0}$ is the chemical potential of component B, under stress-free conditions, for the same concentration as that under stress. w is the strain energy of the solid. N^B is the number of B moles. Therefore the second term in the right-hand side of (5.1), $\partial w/\partial N^B$, represents the strain energy of the solid per mole of component B. Finally W^B is the work performed by the applied stresses, σ_{ij}, per mole of addition of component B. For immobile components, since the addition or removal of the

component takes place at an external surface or an interface, the chemical potential is considered only as a surface property and depends on the orientation of the surface. This is not the case for mobile components. For more details on the significance of the above comments and the respective derivations, the reader is referred to the article by Li et al. (1966).

Relation (5.1) is applied to hydrogen/zirconium solid solution under stress. A material particle of volume, V, is considered, where uniform stresses and strains are assumed:

$$\frac{\partial w}{\partial N^H} = \frac{\partial}{\partial N^H}\left(\int_0^{\varepsilon_{mn}} V\sigma_{ij}d\varepsilon_{ij}\right) = \frac{\partial}{\partial N^H}\left(\int_0^{\sigma_{mn}} V\sigma_{ij}M_{ijkl}d\sigma_{kl}\right) =$$

$$= \int_0^{\sigma_{mn}}\left(\frac{\partial V}{\partial N^H}M_{ijkl}\sigma_{ij} + \frac{\partial M_{rskl}}{\partial \chi^H}\frac{\partial \chi^H}{\partial N^H}V\sigma_{rs}\right)d\sigma_{kl}$$

(5.2)

M_{ijkl} is the elastic compliance tensor of zirconium. Also χ^H is the mole fraction of hydrogen in the solid solution. Assuming that there is no effect of hydrogen on the elastic moduli of the material and taking into account that the derivative of volume with respect to hydrogen moles equals the partial molal volume of hydrogen, $\overline{V}^H$, one may derive from (5.2):

$$\frac{\partial w}{\partial N^H} = \int_0^{\sigma_{mn}}\overline{V}^H M_{ijkl}\sigma_{ij}d\sigma_{kl} = \frac{1}{2}\overline{V}^H M_{ijkl}\sigma_{ij}\sigma_{kl}$$

(5.3)

The work performed by the applied stresses per mole of addition of hydrogen is given by the following relation:

$$W^H = V\sigma_{ij}\frac{\partial \varepsilon_{ij}}{\partial N^H} = V\sigma_{kk}\frac{\overline{V}^H}{3V} = \frac{\sigma_{kk}}{3}\overline{V}^H .$$

(5.4)

Substitution of (5.3) and (5.4) into (5.1) leads to the final expression for the chemical potential of hydrogen, being in solid solution in zirconium under stress:

$$\mu^H = \mu^{H,0} + \overline{V}^H\left(\frac{1}{2}M_{ijkl}\sigma_{ij}\sigma_{kl} - \frac{1}{3}\sigma_{mm}\right)$$

(5.5)

Note that the first term in parenthesis is of the order of σ^2/E, where E is the elastic modulus of zirconium. The second term is of the order of σ. Therefore the second term is significantly larger than the first one. If the first term is neglected, a relation is derived, which is more often used in literature.

The above relations on the chemical potential of mobile and immobile components are used, in the following, for the derivation of hydrogen terminal solid solubility in zirconium under stress.

According to (5.1), hydride chemical potential, in a stressed material, is given by:

$$\mu^{hr} = \mu^{hr,0} + \frac{\partial w}{\partial N^{hr}} - W^{hr},$$ (5.6a)

$$\frac{\partial w}{\partial N^{hr}} = \overline{w}_{acc} + \overline{w}_{int} + \overline{w}_{af},$$ (5.6b)

$$\overline{w}_{acc} = -\frac{1}{2}\int_{\overline{V}^{hr}} \sigma_{ij}^{I} \varepsilon_{ij}^{T} dV,$$ (5.6c)

$$\overline{w}_{int} = -\int_{\overline{V}^{hr}} \sigma_{ij} \varepsilon_{ij}^{T} dV,$$ (5.6d)

$$\overline{w}_{af} = \frac{1}{2}\int_{\overline{V}^{hr}} \sigma_{ij} \varepsilon_{ij} dV,$$ (5.6e)

$$W^{hr} = \sigma_n \overline{V}^{hr}.$$ (5.6f)

$\overline{V}^{hr}$ is the volume of a mole of hydride. In deriving relations (5.6) it was taken into account that hydride formation is accompanied by a deformation, ε_{ij}^{T}, which is mainly a volume expansion. Under no external loading, the above deformation leads to the development of stresses, σ_{ij}^{I}, in the hydride. Under no external loading, material strain energy per mole of precipitating hydride is given by (5.6c), while under externally applied stress, σ_{ij}, the interaction energy (5.6d) as well as the strain energy of the applied field (5.6e), should be also taken into account (Eshelby, 1957). σ_n is the normal stress at the location of solid solution/hydride interface, where the chemical potential is considered.

The chemical potential of stressed zirconium is defined as follows:

$$\mu^{Zr} = \mu^{Zr,0} + \frac{\partial w}{\partial N^{Zr}} - W^{Zr},$$ (5.7a)

$$\frac{\partial w}{\partial N^{Zr}} = \frac{1}{2}\int_{\overline{V}^{Zr}} \sigma_{ij} \varepsilon_{ij} dV,$$ (5.7b)

$$W^{Zr} = \sigma_n \overline{V}^{Zr}.$$ (5.7c)

$\overline{V}^{Zr}$ is the volume of a mole of zirconium.

The hydride, ZrH_x, is in equilibrium with hydrogen and zirconium either under stress or under stress-free conditions. Consequently:

$$\mu^{hr} = \mu^{Zr} + x\mu^{H}\left(C^{TS}\right),$$ (5.8a)

$$\mu^{hr,0} = \mu^{Zr,0} + x\mu^{H,0}\left(C^{TS,0}\right).$$ (5.8b)

$C^{TS}, C^{TS,0}$ is hydrogen terminal solid solubility under applied stress and stress-free conditions, respectively. By substitution of relations (5.6), (5.7) and (5.8b) into (5.8a), one may derive:

$$x\left[\mu^H\left(C^{TS}\right) - \mu^{H,0}\left(C^{TS,0}\right)\right] = \overline{w}_{acc} + \overline{w}_{int} +$$
$$+ \frac{1}{2}\left(\int_{\overline{V}^{hr}} \sigma_{ij}\varepsilon_{ij}dV - \int_{\overline{V}^{Zr}} \sigma_{kl}\varepsilon_{kl}dV\right) - \sigma_n\left(\overline{V}^{hr} - \overline{V}^{Zr}\right) \tag{5.9}$$

It has been implied that hydride and zirconium equilibrium concentrations do not change significantly with stress. Because of material continuity the molal volume of the hydride equals that of the solid solution at the hydride/solid solution interface; consequently $\overline{V}^{hr} \approx \overline{V}^{Zr}$ and the terms of (5.9) in parenthesis vanish. Also in ideal or dilute solutions (Raoult's law), stress-free hydrogen chemical potential satisfies the following well-known relation:

$$\mu^{H,0} = \mu^{H,RS} + RT\ln\left(C^H\overline{V}\right), \tag{5.10}$$

where $\mu^{H,RS}$ is hydrogen chemical potential in the 'standard' (i.e. reference) state. $\overline{V}$ is the molal volume of solid solution. Then, by taking into account (5.10) and substituting (5.5) into (5.9), one derives the terminal solid solubility of hydrogen in zirconium under stress:

$$C^{TS} = C^{TS,0}\exp\left(\frac{\overline{w}_{acc} + \overline{w}_{int}}{xRT}\right)\exp\left[\frac{\overline{V}^H}{RT}\left(\frac{\sigma_{mm}}{3} - \frac{1}{2}M_{ijkl}\sigma_{ij}\sigma_{kl}\right)\right]. \tag{5.11}$$

Puls (1981) followed a different approach, based on Moutier cycle, and derived a simplified expression, which does not include the elastic compliance term.

6. Constitutive Relations for Zirconium Deformation

In the present mathematical formulation all phases are taken as elastic. It is also assumed that the elastic properties of hydride and solid solution are identical and do not depend on hydrogen concentration. The material deformation is coupled with hydrogen diffusion and energy flow due to the strains, which are caused by hydrogen dissolution, hydride formation and thermal expansion:

$$\frac{d\sigma_{ij}}{dt} = M_{ijkl}^{-1}\left(\frac{d\varepsilon_{ij}}{dt} - \frac{d\varepsilon_{ij}^H}{dt} - \frac{d\varepsilon_{ij}^E}{dt}\right), \tag{6.1a}$$

$$M_{ijkl}^{-1} = \lambda\delta_{ij}\delta_{kl} + \mu\left(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}\right), \tag{6.1b}$$

$$\frac{d\varepsilon_{ij}^H}{dt} = \frac{1}{3}\delta_{ij}\frac{d}{dt}\left[f\theta^{hr} + (1-f)C^H\overline{V}^{Zr}\theta^H\right], \tag{6.1c}$$

$$\frac{d\varepsilon_{ij}^{E}}{dt} = a\delta_{ij}\frac{d\mathrm{T}}{dt}.$$
(6.1d)

λ, μ are Lame constants for zirconium. $\theta^{hr} = \varepsilon_{kk}^{T}$ is hydride expansion, occurring during its precipitation. θ^{H} is the expansion of zirconium lattice, when a mole of hydrogen corresponds to a mole of zirconium in solid solution; a relation similar to (6.1c) has been also used by Lufrano et al. (1996). Finally, a is the thermal expansion coefficient of zirconium.

7. Conclusions

Zirconium alloy in fuel cladding of light water reactors is under temperature gradient, during reactor operation. Also the generation of micro-cracks on the external corroded surface introduces significant stress gradients. Consequently the degradation of the material due to hydrogen, generated by oxidation on the external cladding surface, is affected by several interrelated processes, namely: (i) hydrogen diffusion, (ii) non-mechanical energy flow, (iii) hydride formation and (iv) hydride/solid solution deformation.

A mathematical model is presented, which takes into account the coupling of all four processes. Hydrogen diffusion and non-mechanical energy flow are described by the governing equations ((3.2), (3.4)) and ((4.6), (4.9)), respectively. Hydride precipitation occurs when the terminal solid solubility, given by (5.11), is reached. Finally, the constitutive behavior of solid solution / hydride material is described by (6.1).

The above governing equations will be implemented in a finite element algorithm together with a de-cohesion model for crack growth (Varias, 1998), in order to estimate damage growth in zirconium, caused by hydrogen embrittlement.

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