



Chemo-mechanics couplings in polymer matrix materials exposed to thermo-oxidative environments

Couplages oxydation–mécanique dans les résines de type époxy soumises à un environnement dit « haute température »

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ABSTRACT

The present article focuses on the modelling of chemo-mechanics couplings in polymer matrix materials exposed to thermo-oxidative environments at high temperatures (150 °C). The coupling between oxygen reaction–diffusion and mechanics is put in evidence theoretically through the employment of a unified approach, based on the thermodynamics of irreversible processes; it is found that oxygen reaction–diffusion in the polymer matrix can be influenced by the strain tensor, in particular by its trace and by its spatial gradients.

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R É S U M É

Le présent article s'intéresse à la modélisation des couplages entre l'oxydation et la mécanique dans les résines de type époxy soumises à un environnement dit « haute température » (150 °C). Le couplage entre le schéma mécanistique de réaction diffusion de l'oxygène et la mécanique est abordé théoriquement en utilisant une approche classique de la thermodynamique des processus irréversibles. Il est montré que le phénomène de diffusion–réaction peut être influencé par le tenseur des déformations mais aussi par le gradient spatial de la trace des déformations.

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1. Introduction

Aging in fibre reinforced polymer composites is represented by the long-term action of physical, chemical and mechanical phenomena such as creep, water absorption, thermo-oxidation, UV light: polymeric resins are particularly reactive to the environment at high temperatures, while carbon fibres are stable.

In particular, thermo-oxidation is the coupled reaction–diffusion of oxygen occurring in polymer matrices at high temperatures, a chemical process accompanied by the formation of volatile products and the local disruption of the polymer macromolecular chains; these phenomena lead to mass and density variations, irreversible shrinkage strains and may promote a consistent change of the local mechanical properties (Young's modulus, critical stress, fracture toughness, among others).

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The cited effects may give rise in turn to fibre-matrix debonding close to the external surfaces exposed to the environment and promote the onset of matrix microcracking under the thrust of thermo-mechanical solicitations in air or oxygen rich environments [1].

Multi-physical couplings are responsible for such mechanisms and they can be particularly marked when the interaction between polymer materials (and polymer composites) and gas/liquid rich environments is concerned.

Historically, there is a large body of literature (and different approaches) concerning *strong* diffusion–mechanics couplings occurring in water and gas transport in polymeric materials.

For instance, Larché and Cahn [14,15] starting from the Gibbs theory of thermodynamics equilibrium for solid mixtures [16] developed a linearised and a nonlinear theory for “*a solid which absorbs fluids, a material in essence comparable macroscopically to a sponge or microscopically to a gelatine*”, like polymeric materials that absorb solvents, and substitutional solid solutions in which atoms diffuse by a vacancy mechanism.

Truesdell [17] developed a theory of mixtures in which a system is considered as an assembly of different sub-systems occupying the same space at the same time. Each sub-system is allowed to exchange mass, momentum and energy with any other sub-systems but the conservation principles for mass, momentum and energy of the mixture must be respected. Finally, the second law of thermodynamics, expressed through an entropy inequality for the whole mixture should be identically satisfied for any admissible process, given by an arbitrary solution of the cited balance equations.

An improved version of such theory, taking into account materials with memory, has been presented by Lustig et al. [18].

Weitsman [19] and Carbonell and Sarti [20] developed approaches which are intermediate between Gibbs/Larché and Cahn and Truesdell/Lustig. Their approaches are based on the Thermodynamics of Irreversible Processes (TIP) and impose global balances on the whole mixture, which is composed of a solid solvent and a solute, without giving a precise description of the evolution of the sub-systems.

These approaches are for elastic and viscoelastic materials and are explicitly devoted to polymers and polymer-based composites. Their relative simplicity is dictated by the necessity to explain complex experimental phenomena (anomalies in the absorption process) through straightforward and manageable models.

In particular Weitsman [19] shows how an applied or a self-induced stress may assist water diffusion in elastic and viscoelastic materials identifying eventually an *apparent* diffusion coefficient dependent on stress and on the mechanical properties of the materials. The *apparent* diffusivity, in turn, may have a remarkable effect on the solute concentration profiles inside the material, affecting the induced stress.

Recently, Rambert et al. [21,22] Valancon et al. [23], presented coupled numerical models of water and gas transport in polymers based also on TIP, enhancing the direct couplings which may exist between heat transfer, mass transport, chemical reaction and mechanical behaviour. These works put in evidence the complex multi-physical behaviour of polymer materials; diffusion phenomena may driven by stress and, conversely, the elastic and viscoelastic response of polymers may be influenced by diffusion. In particular, water/gas diffusion in the polymeric material may be accelerated by the stress state within the material and follow a path which is oriented by stress gradients.

The literature singles out two possible effects of strain (stress) on mass and species diffusion: the effect of strain (stress) intensity (see, for instance, Larché and Cahn [14,15]) and the effect of the gradient of the strain (stress) tensor (see, for instance, Weitsman [19] and Rambert et al. [21]).

Concerning thermo-oxidation mechanisms in polymers and polymer matrix composites, there is a large body of recent work (see, for instance, Colin et al. [2,3], Decelle et al. [4], McManus et al. [5], Schieffer et al. [6], Tandon et al. [7], Tsotsis et al. [8]); in particular, Colin et al. [2,3] have developed a mechanistic-based scheme which describes thermo-oxidation reaction–diffusion phenomena at the molecular scale.

Olivier et al. [9–12] have contributed validating the mechanistic model by Colin et al. [2,3] and, on the bases of such model have developed a coupled reaction–diffusion–mechanics model within the formalism of TIP. The model is able to catch stress localisation occurring during thermal oxidation and to predict eventually the oxidation induced fibre-matrix debonding. Validation of the model has been provided by Gigliotti et al. [13] through comparison between the predicted and the experimentally measured thermo-oxidation induced shrinkage profiles in IM7/977-2 carbon–epoxy composite materials exposed to oxidative environments.

In all the cited approaches the coupling between reaction–diffusion and mechanics is *weak*; the chemical fields have an effect on the mechanicals ones, but mechanics – the state of strain and stress in the polymeric matrix – has no influence on oxygen reaction–diffusion.

A contribution by Popov et al. [34,35] concerning the ozone–polymer interaction shows that the direct effect of level of stress on the chemical reaction can be considered of the second order.

The question about how to evaluate *strong* chemo-mechanics coupling effects in polymer and composite materials is a quite complex issue, since all experimental tests engender spatial gradients. Moreover, in order to be interpreted, such tests need thus to be guided by a chemo-mechanics coupled model. In particular, such a model should help identifying all the possible forms of couplings and design relevant coupled tests.

The aim of the present article is to assess chemo-mechanics couplings by taking into account different forms of coupling (direct and indirect couplings). More precisely, we want to put into evidence theoretically the influence of the strain tensor and of its spatial gradients on the oxygen reaction–diffusion mechanism. Chemo-mechanics couplings are put into evidence theoretically through the employment of a unified approach, based on TIP (De Groot [24], Prigogine et al. [25]), following a

formalism similar to that developed by Rambert et al. [21,22] and by Rabearison et al. [26] for polymeric resins submitted to curing processes, in which crosslinking reaction phenomena play a primordial role.

The paper is divided as follows: in Section 2 the classical reaction–diffusion model by Colin et al. [2,3] is briefly recalled, reviewing results already published [9–12], and putting into evidence the need for a fully coupled formulation, which is more consistent from a thermodynamics point of view.

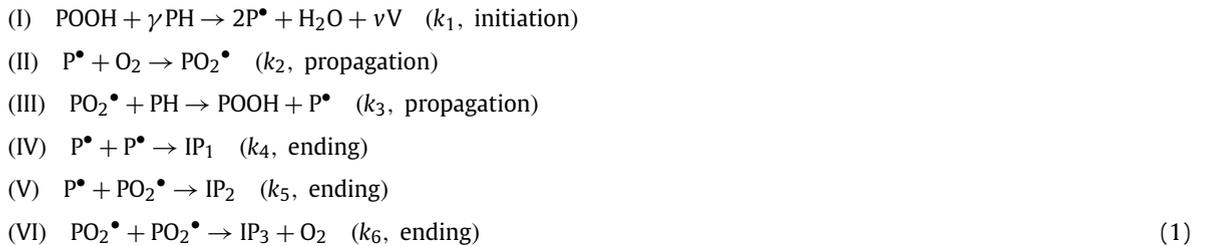
In Section 3 mechanics–diffusion couplings are modelled in a general setting and discussed. In Section 4 conclusions and perspectives are finally presented.

2. Classical mechanistic scheme and its experimental assessment

The present section recalls results which have already been presented in [9–12], with a short introduction to a mechanistic scheme model for thermo-oxidation of epoxy resin based composites developed by Colin et al. [2,3]. This model has been also employed in [13] for validation purposes.

In particular in this section we want to review how chemo-mechanics couplings have been handled out until today within the context of the classical mechanistic scheme.

The classical mechanistic models thermo-oxidation at the molecular scale following the closed loop scheme:



In this scheme the global oxidative reaction generates hydro peroxides POOH reactants and a substrate consumption phenomenon due to PH concentration. The scheme identifies ten different chemical species: POOH, PH, H₂O, V (volatiles), O₂, P[•], PO₂[•] (the symbol [•] identifies free radicals) and three species of inactive products, IP₁, IP₂ and IP₃. Volatiles are composed by different molecules though, for convenience, only one average volatile molecule is considered. Fibres are supposed to be thermally and chemically stable through the whole process.

Assuming that the volatile species escape instantaneously from the material (no volatiles diffusion), the coupled system of differential equations related to the classical mechanistic scheme (1) and governing thermo-oxidation reaction–diffusion is given by:

$$\begin{aligned}
 \frac{\partial [\text{O}_2]}{\partial t} &= -k_2 [\text{P}^\bullet] [\text{O}_2] + k_6 [\text{PO}_2^\bullet]^2 + D_{\text{O}_2} \nabla^2 [\text{O}_2] \\
 \frac{\partial [\text{POOH}]}{\partial t} &= k_3 [\text{PH}] [\text{PO}_2^\bullet] - k_1 [\text{POOH}] \\
 \frac{\partial [\text{PH}]}{\partial t} &= -k_3 [\text{PH}] [\text{PO}_2^\bullet] - \gamma k_1 [\text{POOH}] \\
 \frac{\partial [\text{PO}_2^\bullet]}{\partial t} &= k_2 [\text{P}^\bullet] [\text{O}_2] - k_3 [\text{PH}] [\text{PO}_2^\bullet] - k_5 [\text{PO}_2^\bullet] [\text{P}^\bullet] - 2k_6 [\text{PO}_2^\bullet]^2 \\
 \frac{\partial [\text{P}^\bullet]}{\partial t} &= 2k_1 [\text{POOH}] - k_2 [\text{P}^\bullet] [\text{O}_2] + k_3 [\text{PH}] [\text{PO}_2^\bullet] - 2k_4 [\text{P}^\bullet]^2 - k_5 [\text{PO}_2^\bullet] [\text{P}^\bullet]
 \end{aligned} \tag{2}$$

in which k_1, \dots, k_6 are rate constants and D_{O_2} is the oxygen diffusion coefficient. The first equation of (2) governs oxygen reaction–diffusion, the first term on the right side of the equation being the reaction “source”, the second one being the diffusion term. In order (2) to be solved, initial and boundary conditions must be specified for the species. Usually, the oxygen concentration at the exposed surface is supposed to be related to the external pressure through the classical Henry law:

$$[\text{O}_2]_s = pS \tag{3}$$

in which S is the solubility coefficient. Other sorption laws can be specified for high pressures (see for instance [9]), however the Henry law is appropriate for low pressures.

Oxygen reaction–diffusion is usually characterised by a global parameter, the concentration of oxidation products, Q , defined by:

$$Q(x, y, z, t) = \int_0^t -\frac{d[\text{O}_2]}{d\tau} d\tau \tag{4}$$

Eqs. (1) to (4) describe and simulate the chemical phenomena related to thermo-oxidation in the polymer matrix material. Coupling with mechanics can be achieved in a relatively straightforward way by calculating the shrinkage strains due to the chemical reaction–diffusion phenomena and by employing them as free strains in the mechanical equations (compatibility, equilibrium and constitutive equations). In this case the coupling is *weak* since the chemical fields are calculated independently from mechanics.

According to Colin et al. [2,3] and Decelle et al. [4] volatiles departure is responsible for chemical shrinkage, which engenders mass, density and local volume variations, thus local strain.

The polymer shrinkage strain, \mathbf{E}^{SH} , can be expressed in the following form:

$$\mathbf{E}^{SH} = \frac{1}{3} \frac{\Delta V}{V_0} \mathbf{I} = \frac{1}{3} \left(\frac{\Delta m}{m_0} - \frac{\Delta \rho}{\rho_0} \right) \mathbf{I} \quad (5)$$

in which \mathbf{I} is the second order identity tensor, V and V_0 , m and m_0 , ρ and ρ_0 are the actual and the initial volume, mass and density, respectively. The reader is referred to Refs. [2–4] for further discussion about the terms appearing in Eq. (5).

Residual stresses of thermal, hydrothermal and chemical nature, \mathbf{S} , can be calculated according to the following elastic constitutive equation under the hypothesis of small strain:

$$\mathbf{S} = \mathbb{C} : (\mathbf{E} - \mathbf{E}^T - \mathbf{E}^H - \mathbf{E}^{SH}) \quad (6)$$

in which \mathbf{S} is the stress tensor, \mathbb{C} is the elasticity tensor, \mathbf{E} is the total strain tensor, \mathbf{E}^T and \mathbf{E}^H are the free thermal and hygroscopic expansion strain tensors, respectively. Eq. (6) takes into account through \mathbf{E}^T and \mathbf{E}^H the possible contribution of thermal or hydrothermal free strains.

Eqs. (5) and (6) represent a first form of weak coupling. Strains and stresses are calculated from the oxygen reaction–diffusion equations; the concept of free thermo-oxidation induced polymer shrinkage strain is essential for stress evaluation.

Another form of *weak* chemo-mechanics coupling which may be defined as *indirect* consists in taking into account the effects of the chemical reaction–diffusion phenomena on the material behaviour law of the polymer.

For instance, the thermo-oxidation induced local changes of elastic modulus can be expressed as a function of the concentration of oxidation products, as follows:

$$\mathbb{C} = \mathbb{C}(Q) \quad (7)$$

The parameters of the classical mechanistic scheme can be identified through mass loss tests at several temperatures (see, for instance, [4] and [27]). It is a “global” technique similar to weight testing of resin and composite samples to assess water absorption/desorption.

Another technique, which can be defined as “local” and that has been employed for validation purposes (see, for instance, [10–12]), consists in measuring – at room temperature – the indentation elastic module (EIT) profiles of oxidised resin samples and to relate them to the concentration of oxidation products – Eq. (4). Thanks to these tests, functional relationships of the type (7) can be also identified, at room temperature.

The literature [9–12] shows that the temporal evolution of the EIT spatial profiles – measured at room temperature – correlates well with that of the calculated Q spatial profiles. In particular, the following explicit form for EIT(Q) has been identified (MPa):

$$\text{EIT}(Q) = 5510 - 1469 \exp(-0.48Q) \quad (8)$$

Indentation Elastic Modulus measurements are thus a good way of validating and identifying, locally, the mechanistic scheme and the weakly coupled chemo-mechanics model, since they are able to catch experimentally the evolution of the Q spatial profiles.

Moreover, functional relationships such as (8) can be effectively constructed and identified through EIT measurements.

Once identified, the model can be employed for the simulation and the prediction of the thermo-oxidation induced shrinkage profiles in composite materials exposed to oxidative environments [13].

3. Chemo-mechanics coupled model

As shown in Section 2 two chemo-mechanics couplings effects can be singled out within the context of the classical mechanistic scheme.

The first one is the effect of the chemical reaction on the free chemical shrinkage strain, \mathbf{E}^{SH} (Eq. (5)), the second one is the effect of the chemical reaction on the EIT module (Eqs. (7) and (8)). Both effects have a direct impact on the residual stress state of the polymer (Eq. (6)).

However the direct effect of mechanics on the mechanistic oxygen reaction–diffusion scheme (Eq. (2)) has never been taken into account in the existing literature concerning thermo-oxidation.

A basic question which arises is: which form of chemo-mechanics couplings may exist within the context of TIP and for the particular problem of thermo-oxidation of a polymer matrix.

The present section provides thus an attempt to put into evidence theoretically the chemo-mechanics couplings including *strong* and *direct* couplings.

3.1. Diffusion–mechanics fully coupled model

The assumption of “local equilibrium” is formulated by TIP: each part of a material system can be approximately considered, at each time, as being in thermal equilibrium. In TIP, all the notions which can be precisely defined only at equilibrium in thermostatics (for instance, temperature, entropy or potentials) are postulated.

Considering an elementary volume of matrix as a perfect homogeneous mixture of polymer and mobile chemical species, for instance oxygen, the mass balance of each i th mobile species, of mass fraction Y_i , within an elementary volume can be written as (see, for instance, Prigogine et al. [25] and Germain et al. [29]):

$$\rho \frac{\partial Y_i}{\partial t} = \sum_{r=1}^{n_r} \nu_{ir} M_i w_r - \nabla \cdot \mathbf{j}_{mi} \quad (9)$$

in which ρ is the density, ν_{ir} the stoichiometric coefficient of the r th reaction, M_i the molar mass of the i th species, w_r the r th reaction rate, \mathbf{j}_{mi} the mass flux of the i th species and n_r the total number of reactions.

Eq. (9) may be written in an equivalent form:

$$\frac{\partial Y_i^*}{\partial t} = \sum_{r=1}^{n_r} \nu_{ir} w_r - \frac{1}{M_i} \nabla \cdot \mathbf{j}_{mi} \quad (10)$$

by introducing the molar concentration $Y_i^* = \rho Y_i / M_i$, i.e. the number of moles per unit volume.

In order to develop a fully coupled chemo–mechanics model we make use of a procedure which is typical of TIP and which consists in introducing and defining dissipation and thermodynamic potentials from which the state and the evolution equations can be found by derivation.

In order to construct these potentials first the stress and strain tensor, \mathbf{S} and \mathbf{E} respectively, are decomposed into their spherical ($\mathbf{S}^s, \mathbf{E}^s$) and deviatoric ($\mathbf{E}^d, \mathbf{E}^d$) components:

$$\mathbf{S}^s = \frac{1}{3} \text{tr} \mathbf{S} \mathbf{I}, \quad \mathbf{S}^d = \mathbf{S} - \mathbf{S}^s, \quad \mathbf{E}^s = \frac{1}{3} \text{tr} \mathbf{E} \mathbf{I}, \quad \mathbf{E}^d = \mathbf{E} - \mathbf{E}^s \quad (11)$$

The strain/stress decomposition finds its motivation in the hypothesis – put forward in [28] at the molecular scale – that the oxidation reaction does not influence the bulk modulus K of the epoxy polymer matrix; in this case, only the shear modulus of the polymer depends on the chemical reaction, $G = G(Q)$. It should be also noted that in a linearised setting $\text{tr} \mathbf{E} = \text{tr} \mathbf{E}^{an} + \text{tr} \mathbf{E}^e + \text{tr} \mathbf{E}^T + \text{tr} \mathbf{E}^H + \text{tr} \mathbf{E}^{SH}$, that is, the trace of the total strain tensor (\mathbf{E}) is equal to the sum of the traces of the elastic strain tensor (\mathbf{E}^e), the inelastic strain tensor (\mathbf{E}^{an}) and the thermal (\mathbf{E}^T), hygroscopic (\mathbf{E}^H) and irreversible chemical shrinkage free strain tensors (\mathbf{E}^{SH}), respectively. In turn the free strain tensors can be related to the respective volume relative variations $(\Delta V / V_0)^\beta$ and to the respective Jacobian, \mathbf{J}^β , by relations of the type $\text{tr} \mathbf{E}^\beta = (\Delta V / V_0)^\beta = \mathbf{J}^\beta - 1$.

Linear relations are usually employed so that $\text{tr} \mathbf{E}^\beta = \sum_i \gamma_\beta \Delta \beta$, in which γ_β are coefficients of thermal, hygroscopic or chemical expansion and $\Delta \beta$ is the related variation ($\beta = T, H$ or SH). According to TIP and employing the strain/stress decomposition the generalised Gibbs equation can be written as:

$$T ds = de - \frac{1}{\rho} \text{tr} \mathbf{S} d \text{tr} \mathbf{E} - \frac{1}{\rho} \mathbf{S}^d : d \mathbf{E}^d - \sum_{i=1}^{n_s} \mu_i dY_i + \sum_{j=1}^{n_{iv}} \mathbf{f}_j \cdot d\mathbf{v}_j \quad (12)$$

In Eq. (12) T is the temperature, s the specific entropy per unit mass (J/kgK), e the specific internal energy per unit mass (J/kg), μ_i is the chemical potential of the i th specie (J/kg). \mathbf{v}_j represents a set of internal variables, \mathbf{f}_j are the associated thermodynamic “forces”, n_s is the total number of chemical species and n_{iv} is the total number of internal variables. In Eq. (12) the term $\sum_i \mu_i dY_i$ can be also expressed by the equivalent $\sum_i \frac{1}{\rho} \mu_i^* dY_i^*$ in which $\mu_i^* = \mu_i M_i$ is the chemical potential of the i th specie per unit mole (J/mol).

The second principle can be expressed as follows:

$$\rho \frac{ds}{dt} = \frac{1}{T} \left(\mathbf{S} : \frac{d\mathbf{E}^{an}}{dt} - \nabla \cdot \mathbf{q} + r - \sum_{i=1}^{n_s} \mu_i \left(\sum_{r=1}^{n_r} \nu_{ir} M_i w_r - \nabla \cdot \mathbf{j}_{mi} \right) + \rho \sum_{j=1}^{n_{iv}} \mathbf{f}_j \cdot \frac{d\mathbf{v}_j}{dt} \right) \quad (13)$$

in which \mathbf{q} the heat flux and r the internal heat source. According to Prigogine et al. [25] the entropy variation can be decomposed into an *exchange* term and *internal* term, that is:

$$\begin{aligned} \rho \frac{de_s}{dt} &= -\nabla \cdot \left(\frac{1}{T} \left(\mathbf{q} - \sum_{i=1}^{n_s} \mu_i \mathbf{j}_{mi} \right) \right) + \frac{1}{T} r \\ \rho \frac{di_s}{dt} &= 1/T \mathbf{S} : \frac{d\mathbf{E}^{an}}{dt} + \mathbf{q} \cdot \nabla \frac{1}{T} + \left(\frac{1}{T} \right) \sum_{r=1}^{n_r} A_r w_r - \sum_{i=1}^{n_s} \mathbf{j}_{mi} \cdot \nabla \frac{\mu_i}{T} + \rho/T \sum_{j=1}^{n_{iv}} \mathbf{f}_j \cdot \frac{d\mathbf{v}_j}{dt} \end{aligned} \quad (14)$$

the internal term is due to internal dissipation due to irreversible phenomena, the exchange term includes heat flux terms that compensate the entropy variation promoted by internal dissipation. The internal dissipation term must be greater than zero for irreversible transformation, while it is equal to zero for reversible transformations.

In Eq. (14) A_r defined by:

$$A_r = - \sum_{k=1}^{n_s} \nu_{kr} M_k \mu_k = - \sum_{k=1}^{n_s} \nu_{kr} \mu_k^* \tag{15}$$

represents the “affinity”, in the sense of De Donder [25,29].

In the present context internal dissipation terms due to inelastic strains and internal variables can be discarded, therefore, by introducing the entropy flux term \mathbf{j}_S as follows:

$$\mathbf{j}_S = \frac{1}{T} \left(\mathbf{q} - \sum_{i=1}^{n_s} \mu_i \mathbf{j}_{mi} \right) \tag{16}$$

the *dissipation*, Φ , is finally given by:

$$\Phi = -\mathbf{j}_S \cdot \nabla T + \sum_{r=1}^{n_r} A_r w_r - \sum_{i=1}^{n_s} \mathbf{j}_{mi} \cdot \nabla \mu_i \tag{17}$$

It is interesting to note [30,31] that the dissipation can be written in synthetic form as the product of a generalised thermodynamic force and a generalised thermodynamic velocity:

$$\Phi = \mathbf{y} \cdot \dot{\mathbf{z}} \geq 0 \tag{18}$$

Then, following Lord Rayleigh [32], assuming the existence of a *dissipation function*, $D(\dot{\mathbf{z}})$, which is function of the generalised velocities, and of its Legendre–Frenchel transform, $D^*(\mathbf{y})$, function of the generalised forces, it is possible to deduce generalised forces and generalised velocities in a straightforward way, through:

$$\mathbf{y} = \frac{\partial D}{\partial \dot{\mathbf{z}}}, \quad \dot{\mathbf{z}} = \frac{\partial D^*}{\partial \mathbf{y}} \tag{19}$$

In the present context the dissipation function and its Legendre–Frenchel transform can be written:

$$D = D(\mathbf{j}_S, w_r, \mathbf{j}_{mi}), \quad D^* = D^*(-\nabla T, A_r, -\nabla \mu_i) \tag{20}$$

By defining an equivalent strain $\mathbf{E}^* = \mathbf{E}^d : \mathbf{E}^d$ and by choosing a quadratic dissipation potential, being close to thermodynamic equilibrium:

$$\begin{aligned} D^* &= \frac{1}{2} (-\nabla T) \cdot \mathbf{B}_T (\text{tr} \mathbf{E}, \mathbf{E}^*) \cdot (-\nabla T) + \frac{1}{2} \sum_{r=1}^{n_r} B_r (\text{tr} \mathbf{E}, \mathbf{E}^*) A_r^2 \\ &+ \frac{1}{2} \sum_{i=1}^{n_s} (-\nabla \mu_i) \cdot \mathbf{B}_{\mu i} (\text{tr} \mathbf{E}, \mathbf{E}^*) \cdot (-\nabla \mu_i) + \sum_{i=1}^{n_s-1} \sum_{j=1}^{n_s} (-\nabla \mu_i) \cdot \mathbf{C}_{\mu ij} (\text{tr} \mathbf{E}, \mathbf{E}^*) \cdot (-\nabla \mu_j) \end{aligned} \tag{21}$$

in which \mathbf{B}_T , B_r and $\mathbf{B}_{\mu i}$, $\mathbf{C}_{\mu ij}$ are strain-dependent coefficients associated, respectively, to heat transfer, chemical reaction and diffusion, the reaction rate and mass flux are finally given by:

$$\begin{aligned} w_r &= \frac{\partial D^*}{\partial A_r} = B_r (\text{tr} \mathbf{E}, \mathbf{E}^*) A_r = -B_r (\text{tr} \mathbf{E}, \mathbf{E}^*) \sum_{k=1}^{n_s} \nu_{kr} M_k \mu_k = -B_r (\text{tr} \mathbf{E}, \mathbf{E}^*) \sum_{k=1}^{n_s} \nu_{kr} \mu_k^* \\ \mathbf{j}_{mi} &= \frac{\partial D^*}{\partial (-\nabla \mu_i)} = -\mathbf{B}_{\mu i} (\text{tr} \mathbf{E}, \mathbf{E}^*) \cdot \nabla \mu_i - \mathbf{C}_{\mu ij} (\text{tr} \mathbf{E}, \mathbf{E}^*) \cdot (-\nabla \mu_j) \\ &= -\frac{\mathbf{B}_{\mu i} (\text{tr} \mathbf{E}, \mathbf{E}^*)}{M_i} \cdot \nabla \mu_i^* - \frac{\mathbf{C}_{\mu ij} (\text{tr} \mathbf{E}, \mathbf{E}^*)}{M_j} \cdot \nabla \mu_j^* \end{aligned} \tag{22}$$

Eq. (22a) expresses the reaction rate w_r as a function of the chemical potential. Eq. (22b) relates the mass flux to the gradient of the chemical potential. It has to be noted that by Eqs. (21) and (22b) the mass flux of the i th species is related not only to the gradient of its own chemical potential (Fick’s first law) but also to the gradient of the chemical potential of the j th species (with $j \neq i$). The tensor $\mathbf{C}_{\mu ij}$ relates the mass flux of the i th species to the gradient of the chemical potential of the j th species.

By substituting (22a) and (22b) into (10) gives:

$$\begin{aligned} \frac{\partial Y_i^*}{\partial t} &= \sum_{r=1}^{n_r} v_{ir} (B_r(\text{tr} \mathbf{E}, \mathbf{E}^*) A_r) - \frac{1}{M_i} \nabla \cdot \left(-\frac{\mathbf{B}_{\mu_i}(\text{tr} \mathbf{E}, \mathbf{E}^*)}{M_i} \cdot \nabla \mu_i^* \right) - \frac{1}{M_i} \nabla \cdot \left(-\frac{\mathbf{C}_{\mu_{ij}}(\text{tr} \mathbf{E}, \mathbf{E}^*)}{M_j} \cdot \nabla \mu_j^* \right) \\ &= \sum_{r=1}^{n_r} v_{ir} \left(-B_r(\text{tr} \mathbf{E}, \mathbf{E}^*) \sum_{k=1}^{n_s} v_{kr} \mu_k^* \right) - \frac{1}{M_i} \nabla \cdot \left(-\frac{\mathbf{B}_{\mu_i}(\text{tr} \mathbf{E}, \mathbf{E}^*)}{M_i} \cdot \nabla \mu_i^* \right) \\ &\quad - \frac{1}{M_i} \nabla \cdot \left(-\frac{\mathbf{C}_{\mu_{ij}}(\text{tr} \mathbf{E}, \mathbf{E}^*)}{M_j} \cdot \nabla \mu_j^* \right) \end{aligned} \quad (23)$$

Eq. (23) expresses the general form of the mass balance equation for each i th mobile species, dependent on the choice of the chemical potential per unit mole, μ_i^* . Obviously, Eq. (23) must be solved with the adequate boundary conditions, which will be discussed later.

By an opportune choice of μ_i^* , it is possible to recover the system of Eqs. (2) of the classical mechanistic scheme by the general expression (23). For instance, if the chemical potential of the i th species is proportional to its own concentration, and the mass flux of the i th species does not depend on the gradient of the chemical potential of the j th species (with $j \neq i$), Eq. (22b) corresponds to the so-called second Fick's law which is employed in the classical mechanistic scheme (the diffusion term in the first of Eqs. (2)), as will be detailed later.

Now we search for a general expression for μ_i^* , dependent on the strain tensor, in order to put into evidence the direct chemo-mechanics couplings in Eqs. (23). Once a suitable law for μ_i^* is identified, we apply it to the chemical mechanistic scheme of thermo-oxidation (1) to recover the fully coupled partial differential equations that govern the thermo-oxidative reaction-diffusion phenomenon.

In order to identify a proper form for μ_i^* , it is necessary to introduce a thermodynamic potential, a scalar function of all the state variables and of the internal variables, if any.

The introduction of a thermodynamic potential helps specifying a "collection" of state equations, including proper expressions for the chemical potential of each species and material constitutive relations.

It is useful to remind that thermodynamic potentials can be rigorously defined only at equilibrium. However, since classical TIP concerns *near* equilibrium processes it is reasonable to suppose that even outside equilibrium potentials can be defined as functions of the same variables at equilibrium. Moreover, each part of a material system, at each time, can be approximately considered in thermal equilibrium. These assumptions form the basis of the axiom of local state.

The specific Helmholtz free energy per unit mass (J/kg), ψ , is then taken quadratic, convex with respect to the state variables (the trace of the total strain tensor, $\text{tr} \mathbf{E}$, its deviatoric part, \mathbf{E}^d , the mass fraction, Y_i or, equivalently, the molar concentration, Y_i^*) and to the internal variables (if any) and concave with respect to the temperature; the temperature dependency will not be written explicitly (isothermal conditions only are studied in the present context) in order to simplify calculations:

$$\psi = \psi(\text{tr} \mathbf{E}, \mathbf{E}^d, Y_i^*) \quad (24)$$

For example, the thermodynamic potential may be expressed as:

$$\begin{aligned} \psi(\text{tr} \mathbf{E}, \mathbf{E}^d, Y_i^*) &= \frac{1}{\rho} \left(\frac{3}{2} K (\text{tr} \mathbf{E})^2 + G(Q(Y_i^*)) \mathbf{E}^* \right) \\ &\quad + \sum_{i=1}^{n_s} \frac{1}{\rho} (C_i \text{tr} \mathbf{E} Y_i^* + \alpha_i(\text{tr} \mathbf{E}, \mathbf{E}^*) RT (Y_i^* (\ln(Y_i^*/Y_i^{*0}) - 1)) + \mu_i^{0*} Y_i^*) \end{aligned} \quad (25)$$

in which K is the bulk modulus, $G(Q(Y_i^*))$ the reaction dependent shear modulus, $\alpha_i(\text{tr} \mathbf{E}, \mathbf{E}^*)$, C_i are chemo-mechanics coupling coefficients to be identified. In particular $\alpha_i(\text{tr} \mathbf{E}, \mathbf{E}^*)$ is a strain-dependent coefficient related to the solubility, which plays a role in the sorption process, as we will see later. Finally μ_i^{0*} is a reference chemical potential which may depend on temperature and pressure (standard conditions) but does not depend on molar concentration and Y_i^{*0} is a reference molar concentration so that the ratio (Y_i^*/Y_i^{*0}) corresponds to the *chemical activity* of the i th species. It should be noted that, in Eq. (25), the molar concentration Y_i^* corresponds to the chemical activity of the i th species by assuming a reference molar concentration Y_i^{*0} equal to 1 (mol m^{-3} if Y_i^* is expressed in mol m^{-3}).

The state laws, including an expression for the chemical potential, can be recovered from ψ , as follows:

$$\begin{aligned} \text{tr} \mathbf{S} &= \frac{\partial \rho \psi}{\partial \text{tr} \mathbf{E}} = 3K \text{tr} \mathbf{E} + \sum_{i=1}^{n_s} \left(\frac{\partial \alpha_i(\text{tr} \mathbf{E}, \mathbf{E}^*)}{\partial \text{tr} \mathbf{E}} RT (Y_i^* (\ln(Y_i^*) - 1)) + C_i Y_i^* \right) \\ \mathbf{S}^d &= \frac{\partial \rho \psi}{\partial \text{tr} \mathbf{E}^d} = 2G(Q(Y_i^*)) \mathbf{E}^d + 2 \sum_{i=1}^{n_s} \left(\frac{\partial \alpha_i(\text{tr} \mathbf{E}, \mathbf{E}^*)}{\partial \mathbf{E}^*} RT (Y_i^* (\ln(Y_i^*) - 1)) \right) \mathbf{E}^d \end{aligned}$$

$$\mu_i^* = \frac{\partial \rho \psi}{\partial Y_i^*} = \frac{\partial G(Q(Y_i^*))}{\partial Y_i^*} \mathbf{E}^* + C_i \operatorname{tr} \mathbf{E} + \alpha_i(\operatorname{tr} \mathbf{E}, \mathbf{E}^*) RT \ln Y_i^* + \mu_i^{0*} \quad (26)$$

By substituting Eq. (26c) into Eq. (15) the affinity A_r becomes:

$$A_r = - \sum_{k=1}^{n_s} \nu_{kr} \mu_k^* = - \sum_{k=1}^{n_s} \nu_{kr} \left(\frac{\partial G(Q(Y_k^*))}{\partial Y_k^*} \mathbf{E}^* + C_k \operatorname{tr} \mathbf{E} + \alpha_k(\operatorname{tr} \mathbf{E}, \mathbf{E}^*) RT \ln Y_k^* + \mu_k^{0*} \right) \quad (27)$$

By substituting Eq. (26c) into (23) the mass balance of each i th mobile species, of molar concentration Y_i^* , within an elementary volume can be written as:

$$\begin{aligned} \frac{\partial Y_i^*}{\partial t} = & \sum_{r=1}^{n_r} \nu_{ir} \left(-B_r(\operatorname{tr} \mathbf{E}, \mathbf{E}^*) \sum_{k=1}^{n_s} \nu_{kr} \left(\frac{\partial G(Q(Y_k^*))}{\partial Y_k^*} \mathbf{E}^* + C_k \operatorname{tr} \mathbf{E} + \alpha_k(\operatorname{tr} \mathbf{E}, \mathbf{E}^*) RT \ln Y_k^* + \mu_k^{0*} \right) \right) \\ & - \frac{1}{M_i} \nabla \cdot \left(- \frac{\mathbf{B}_{\mu_i} \alpha_i(\operatorname{tr} \mathbf{E}, \mathbf{E}^*)}{M_i} \cdot \nabla \left(\frac{\partial G(Q(Y_i^*))}{\partial Y_i^*} \mathbf{E}^* + C_i \operatorname{tr} \mathbf{E} + \alpha_i(\operatorname{tr} \mathbf{E}, \mathbf{E}^*) RT \ln Y_i^* + \mu_i^{0*} \right) \right) \\ & - \frac{1}{M_i} \nabla \cdot \left(- \frac{\mathbf{C}_{\mu_{ij}} \alpha_i(\operatorname{tr} \mathbf{E}, \mathbf{E}^*)}{M_j} \cdot \nabla \left(\frac{\partial G(Q(Y_j^*))}{\partial Y_j^*} \mathbf{E}^* + C_j \operatorname{tr} \mathbf{E} + \alpha_j(\operatorname{tr} \mathbf{E}, \mathbf{E}^*) RT \ln Y_j^* + \mu_j^{0*} \right) \right) \end{aligned} \quad (28)$$

Eq. (28) describes reaction–diffusion of the i th species and is characterised by the sum of three terms. The first one is the reaction term; the second one is a diffusion term dependent on the gradient of the chemical potential of the i th species itself, the third one is a diffusion term depending on the gradient of the chemical potential of the j th species.

In particular, concerning the reaction part,

- $B_r(\operatorname{tr} \mathbf{E}, \mathbf{E}^*)$ is a reaction coefficient which may depend on the strain tensor,
- the term $\sum_{k=1}^{n_s} \nu_{kr} \frac{\partial G(Q(Y_k^*))}{\partial Y_k^*} \mathbf{E}^*$ follows from the dependency of G on Q thus on Y_i^* , which has been proven experimentally in Section 2. This term must be present at least theoretically,
- the term $C_k \operatorname{tr} \mathbf{E}$ is homologous to the chemical shrinkage strain term in Eq. (31) whose existence is proved experimentally; therefore this term should be present at least theoretically,
- the term $\alpha_i(\operatorname{tr} \mathbf{E}, \mathbf{E}^*) RT \ln Y_i^*$ is specific to the chemical reaction and is essential to construct the mechanistic scheme, as it will be shown later. It should be noted that α_i may depend on strain.

The diffusion part is characterised by the spatial gradients of both chemical and mechanical quantities, still involving the deviatoric part and the trace of the strain tensor, \mathbf{E}^* and $\operatorname{tr} \mathbf{E}$ respectively, and a classical diffusion term, depending on the species concentration, Y_i^* .

The last diffusion term, involving the strain dependent tensor $\mathbf{C}_{\mu_{ij}}$, is relevant when coupling between the fluxes of different mobile chemical species does exist.

Boundary conditions for Eq. (28) can be found by imposing – at the interface between the environment and the “solvent” material – the equality of the chemical potentials of the gaseous species and of the species dissolved within the material.

The chemical potential of the gaseous species, μ_g^* , can be classically written:

$$\mu_g^* = \mu_g^{0*} + RT \ln(p/p^0) \quad (29)$$

where μ_g^{0*} is the gas reference potential, p is the gas pressure and p^0 is a reference pressure. The chemical potential μ_{is}^* of a species dissolved within the material at the interface with the environment, (Y_{is}^*) can be written (following Eq. (26c)):

$$\mu_{is}^* = \frac{\partial G(Q(Y_{is}^*))}{\partial Y_{is}^*} \mathbf{E}^* + C_{is} \operatorname{tr} \mathbf{E} + \alpha_{is}(\operatorname{tr} \mathbf{E}, \mathbf{E}^*) RT \ln(Y_{is}^*/Y_{is}^{*0}) + \mu_{is}^{0*} \quad (30)$$

We remark that when Eq. (30) does not depend on \mathbf{E}^* and $\operatorname{tr} \mathbf{E}$ – and with $\mu_g^{0*} = \mu_{is}^{0*}$ – we may recover interface boundary conditions which are analogous to the classical Henry’s law.

As a last general remark we note that \mathbf{E}^* and $\operatorname{tr} \mathbf{E}$ may be the effect of an external applied strain/stress or the result of the self-generated strains/stresses related to the reaction–diffusion process itself through the free chemical shrinkage strain, \mathbf{E}^{SH} .

The former case is usually referred in the literature as *stress-assisted* diffusion.

The second case is usually referred in the literature as *self-assisted* diffusion.

3.2. Recovery of the classical mechanistic scheme for thermo-oxidation

In order to recover the mechanistic scheme by Colin et al. [2], Eq. (2), some assumption should be made, that is:

- only one mobile species must be considered, thus the tensor $\mathbf{C}_{\mu_{ij}}$ must be zero,

- the chemical reaction is not affected by mechanics, therefore the B_r and the \mathbf{B}_{μ_i} coefficients are constant,
- the terms $\sum_{k=1}^{n_s} \nu_{kr} \frac{\partial G(Q(Y_k^*))}{\partial Y_k^*} \mathbf{E}^*$ and $C_k \text{tr} \mathbf{E}$ and its spatial gradients are assumed to be negligible,
- the coefficients $\alpha_i(\text{tr} \mathbf{E}, \mathbf{E}^*)$ do not depend on the strain components.

By Eq. (27) the affinity A_r becomes in this case:

$$A_r = - \sum_{k=1}^{n_s} \nu_{kr} \mu_k^* = - \sum_{k=1}^{n_s} \nu_{kr} (\alpha_k RT \ln Y_k^* + \mu_k^{0*}) \quad (31)$$

The affinity related to each reaction is equal to zero at equilibrium so that:

$$\begin{aligned} A_r &= RT \ln \frac{K(T, p)}{(Y_1^*)^{\nu_{1r} \alpha_1} (Y_2^*)^{\nu_{2r} \alpha_2} \dots (Y_{n_s}^*)^{\nu_{n_s r} \alpha_{n_s}}} \\ &= RT \ln \frac{((Y_1^*)^{\nu_{1r} \alpha_1})_{\text{eq}} ((Y_2^*)^{\nu_{2r} \alpha_2})_{\text{eq}} \dots ((Y_{n_s}^*)^{\nu_{n_s r} \alpha_{n_s}})_{\text{eq}}}{(Y_1^*)^{\nu_{1r} \alpha_1} (Y_2^*)^{\nu_{2r} \alpha_2} \dots (Y_{n_s}^*)^{\nu_{n_s r} \alpha_{n_s}}} \end{aligned} \quad (32)$$

where:

$$\ln K(T, p) = - \frac{\sum_{k=1}^{n_s} \nu_{kr} \mu_k^{0*}}{RT} \quad (33)$$

or, equivalently:

$$K(T, p) = ((Y_1^*)^{\nu_{1r} \alpha_1})_{\text{eq}} ((Y_2^*)^{\nu_{2r} \alpha_2})_{\text{eq}} \dots ((Y_{n_s}^*)^{\nu_{n_s r} \alpha_{n_s}})_{\text{eq}} \quad (34)$$

in which the subscript eq represents equilibrium values.

Then, Eq. (28) becomes:

$$\frac{\partial Y_i^*}{\partial t} = \sum_{r=1}^{n_r} \nu_{ir} \left(-B_r \sum_{k=1}^{n_s} \nu_{kr} (\alpha_k RT \ln Y_k^* + \mu_k^{0*}) \right) - \frac{1}{M_i} \nabla \cdot \left(-\frac{\mathbf{B}_{\mu_i}}{M_i} \cdot \nabla (\alpha_i RT \ln Y_i^* + \mu_i^{0*}) \right) \quad (35)$$

or, equivalently, in terms of the affinity, A_r :

$$\frac{\partial Y_i^*}{\partial t} = \sum_{r=1}^{n_r} \nu_{ir} (B_r A_r) - \frac{1}{M_i} \nabla \cdot \left(-\frac{\mathbf{B}_{\mu_i}}{M_i} \cdot \nabla (\alpha_i RT \ln Y_i^* + \mu_i^{0*}) \right) \quad (36)$$

that is:

$$\begin{aligned} \frac{\partial Y_i^*}{\partial t} &= \sum_{r=1}^{n_r} \nu_{ir} \left(B_r RT \ln \frac{((Y_1^*)^{\nu_{1r} \alpha_1})_{\text{eq}} ((Y_2^*)^{\nu_{2r} \alpha_2})_{\text{eq}} \dots ((Y_{n_s}^*)^{\nu_{n_s r} \alpha_{n_s}})_{\text{eq}}}{(Y_1^*)^{\nu_{1r} \alpha_1} (Y_2^*)^{\nu_{2r} \alpha_2} \dots (Y_{n_s}^*)^{\nu_{n_s r} \alpha_{n_s}}} \right) \\ &\quad - \frac{1}{M_i} \nabla \cdot \left(-\frac{\mathbf{B}_{\mu_i}}{M_i} \cdot \nabla (\alpha_i RT \ln Y_i^* + \mu_i^{0*}) \right) \end{aligned} \quad (37)$$

In the classical mechanistic scheme only oxygen diffusion is considered; therefore $\mathbf{B}_{\mu_{O_2}} \neq 0$. Then, the oxygen reaction-diffusion equation (the first equation of the set of Eqs. (2)) can be recovered by considering reactions II and VI of the scheme in Eq. (1), that is:

$$\begin{aligned} \frac{\partial [O_2]}{\partial t} &= RT \left\{ \nu_{O_2-2} \left[B_2 \ln \frac{([P^*]^{\nu_{p^*}-2} \alpha_{p^*})_{\text{eq}} ([O_2]^{\nu_{O_2-2} \alpha_{O_2}})_{\text{eq}} ([PO_2^*]^{\nu_{PO_2^*} \alpha_{PO_2^*}})_{\text{eq}}}{([P^*]^{\nu_{p^*}-2} \alpha_{p^*}) ([O_2]^{\nu_{O_2-2} \alpha_{O_2}}) ([PO_2^*]^{\nu_{PO_2^*} \alpha_{PO_2^*}})} \right] \right. \\ &\quad \left. + \nu_{O_2-6} \left[B_6 \ln \frac{([PO_2^*]^{\nu_{PO_2^*}-6} \alpha_{PO_2^*})_{\text{eq}} ([PO_2^*]^{\nu_{PO_2^*}-6} \alpha_{PO_2^*})_{\text{eq}} ([IP_3]^{\nu_{IP_3} \alpha_{IP_3}})_{\text{eq}} ([O_2]^{\nu_{O_2-2} \alpha_{O_2}})_{\text{eq}}}{([PO_2^*]^{\nu_{PO_2^*}-6} \alpha_{PO_2^*}) ([PO_2^*]^{\nu_{PO_2^*}-6} \alpha_{PO_2^*}) ([IP_3]^{\nu_{IP_3} \alpha_{IP_3}}) ([O_2]^{\nu_{O_2-2} \alpha_{O_2}})} \right] \right\} \\ &\quad - \frac{1}{M_{O_2}} \nabla \cdot \left(-\frac{\mathbf{B}_{\mu_{O_2}}}{M_{O_2}} \cdot \nabla (\alpha_{O_2} RT \ln [O_2] + \mu_{O_2}^{0*}) \right) \end{aligned} \quad (38)$$

in which $[IP_3]$ represents the concentration of the inactive products IP_3 appearing in reaction VI.

In order to recover the mechanistic scheme it is necessary to further hypothesise that all the α_i involved in all reactions are equal to unity. Then, by following a procedure which is classical in chemical thermodynamics (see for instance Lebon et al. [33]) and which considers chemical processes occurring close to equilibrium conditions equation (38) becomes:

$$\begin{aligned} \frac{\partial [O_2]}{\partial t} &= \frac{RT B_2}{[PO_2^*]_{\text{eq}}} ([PO_2^*]) - \frac{RT B_2}{[P^*]_{\text{eq}} [O_2]_{\text{eq}}} ([P^*] [O_2]) + \frac{RT B_6}{[PO_2^*]_{\text{eq}}^2} ([PO_2^*]^2) \\ &\quad + \frac{RT B_6}{[IP_3]_{\text{eq}} [O_2]_{\text{eq}}} ([IP_3] [O_2]) + \frac{\mathbf{B}_{\mu_{O_2}} RT}{M_{O_2}^2 [O_2]_{\text{eq}}} \nabla \cdot \nabla ([O_2]) \end{aligned} \quad (39)$$

in which the molar concentration values $[X]$ now represent – for each considered species – a small variation with respect to an equilibrium condition.

We note that – in order to recover the mechanistic scheme (the first of Eqs. (2)) from Eq. (39):

- the inverse reaction terms $\frac{RTB_2}{[PO_2^*]_{eq}}([PO_2^*])$ and $\frac{RTB_6}{[IP_3]_{eq}[O_2]_{eq}}([IP_3][O_2])$ are discarded,
- the term $\frac{RTB_2}{[P^*]_{eq}[O_2]_{eq}}$ corresponds to the k_2 constant employed in the mechanistic scheme,
- the term $\frac{RTB_6}{[PO_2^*]_{eq}}$ corresponds to the k_6 constant employed in the mechanistic scheme,
- the term $\frac{B_{\mu O_2}RT}{M_{O_2}^2[O_2]_{eq}}$ corresponds to the D_{O_2} constant employed in the mechanistic scheme; therefore, in such scheme, the diffusion coefficient should depend on the oxygen molar concentration at equilibrium.

Eq. (39) must be solved with opportune boundary conditions, which are found by imposing – at the interface between the environment and the “solvent” material – the equality of the chemical potentials of the gaseous oxygen and of the oxygen dissolved within the material.

In particular, by employing Eqs. (29) and (30), by ignoring the dependency on E^* and $\text{tr}E$ – and with $\mu_g^{0*} = \mu_{[O_2]_s}^{0*}$ – we may recover the classical Henry’s law, Eq. (3), with the solubility coefficient, S , given by:

$$S = \frac{[O_2]_s^0}{p_0 \exp(\alpha_{[O_2]_s})} \quad (40)$$

3.3. Extension of the classical mechanistic scheme by including strong chemo-mechanics couplings

At this stage of the development it is possible to generalise the mechanistic scheme by Colin et al. [2,3], taking into account coupling with mechanics. Without losing generality, only oxygen diffusion is considered, as in Section 3.2: therefore $C_{\mu ij} = 0$ and $B_{\mu O_2} \neq 0$.

Eq. (28) becomes:

$$\begin{aligned} \frac{\partial [O_2]}{\partial t} = & \left\{ \nu_{O_2-2} \left(-B_2(\text{tr}E, E^*) \sum_{k=1}^{n_s} \nu_{kr} \left(\frac{\partial G(Q(Y_k^*))}{\partial Y_k^*} E^* + C_k \text{tr}E + \alpha_k(\text{tr}E, E^*) RT \ln Y_k^* + \mu_k^{0*} \right) \right) \right. \\ & + \nu_{O_2-6} \left(-B_6(\text{tr}E, E^*) \sum_{k=1}^{n_s} \nu_{kr} \left(\frac{\partial G(Q(Y_k^*))}{\partial Y_k^*} E^* + C_k \text{tr}E + \alpha_k(\text{tr}E, E^*) RT \ln Y_k^* + \mu_k^{0*} \right) \right) \left. \right\} \\ & + \frac{B_{\mu O_2}(\text{tr}E, E^*)}{M_{O_2}^2} \nabla \cdot \nabla \left(\frac{\partial G(Q([O_2]))}{\partial [O_2]} E^* + C_{O_2} \text{tr}E + \alpha_{O_2}(\text{tr}E, E^*) RT \ln [O_2] + \mu_{[O_2]}^{0*} \right) \end{aligned} \quad (41)$$

Again Eq. (41) must be solved by imposing opportune boundary conditions such as those specified in Section 3.1, Eqs. (29) and (30).

In Eq. (41) chemo-mechanics couplings appear in several different forms.

The dependency of G on $Q([O_2])$, which is proven experimentally makes the term $\frac{\partial G(Q([O_2]))}{\partial [O_2]} E^*$ appearing in Eq. (41).

However, since E^* follows from a product of strain tensors and we are within the framework of the small strain hypothesis, these terms can be neglected in a first approximation. Moreover the variation of G with respect to the concentration of oxidation products (Eq. (8)) is quite weak.

By ignoring the $\frac{\partial G(Q([O_2]))}{\partial [O_2]} E^*$ term Eq. (41) and its boundary condition (30) can be written, respectively:

$$\begin{aligned} \frac{\partial [O_2]}{\partial t} = & \left\{ \nu_{O_2-2} \left(-B_2(\text{tr}E, E^*) \sum_{k=1}^{n_s} \nu_{kr} (C_k \text{tr}E + \alpha_k(\text{tr}E, E^*) RT \ln Y_k^* + \mu_k^{0*}) \right) \right. \\ & + \nu_{O_2-6} \left(-B_6(\text{tr}E, E^*) \sum_{k=1}^{n_s} \nu_{kr} (C_k \text{tr}E + \alpha_k(\text{tr}E, E^*) RT \ln Y_k^* + \mu_k^{0*}) \right) \left. \right\} \\ & + \frac{B_{\mu O_2}(\text{tr}E, E^*)}{M_{O_2}^2} + \nabla \cdot \nabla (C_{O_2} \text{tr}E + \alpha_{O_2}(\text{tr}E, E^*) RT \ln [O_2] + \mu_{[O_2]}^{0*}) \end{aligned} \quad (42)$$

$$\mu_{[O_2]_s}^* = C_{[O_2]_s} \text{tr}E + \alpha_{[O_2]_s}(\text{tr}E, E^*) RT \ln ([O_2]_s/[O_2]_s^0) + \mu_{[O_2]_s}^{0*} \quad (43)$$

Chemistry kinetics is dependent on $\text{tr}E$ and E^* through the coefficients B_2 , B_6 and α_i .

On the other hand diffusion kinetics is influenced by mechanics through the term $B_{\mu O_2}$.

The $\text{tr}E$ term influences directly the chemical reaction through the $C_k \text{tr}E$ terms and modifies the diffusion path through the $\nabla \cdot \nabla (C_{O_2} \text{tr}E)$ term.

The $\text{tr}E$ term influences also the boundary condition through the $C_{[O_2]_s}$ coefficient.

Eq. (41) presents a certain degree of complexity and must be solved numerically also due to the presence of a boundary condition explicitly depending on strain.

At this stage of the theoretical development we may think about possible experimental tests to be done in order to quantify thermo-oxidation chemo-mechanics couplings.

Two “families” of tests should be conceived; the first test should be done by imposing a uniform strain field on the material sample in order to evaluate the effect of the magnitude of the $\text{tr} \mathbf{E}$ and E^* terms on the oxygen reaction–diffusion. This test should be, in turn, performed on thin *and* thick samples in order to check the effect of mechanics on the sorption process (sample saturation) and on the diffusion process, respectively.

A second test should be performed on samples subjected to strain gradients in order to enhance the effect of such gradients on the diffusion path.

As shown in Section 2, Indentation Elastic Modulus measurements are able to catch experimentally the evolution of the Q spatial profiles, they have been proven effective for validating the classical thermo-oxidation mechanistic scheme.

The idea is to employ the same technique in samples thermo-oxidised under an applied external strain/stress.

Results from an experimental activity on chemo-mechanics couplings employing EIT measurements in polymer thermo-oxidised resins will be the object of a future communication by the authors.

4. Conclusions and perspectives

The aim of the present article was to construct and to assess a chemo-mechanics coupled model for polymer matrix materials exposed to thermo-oxidative environments at high temperature, in which oxygen reaction–diffusion phenomena take place.

In order to do this, first, an uncoupled mechanistic scheme of oxygen reaction–diffusion operating at the molecular scale has been presented in its “classical” form (Colin et al. [2]). Moreover a way to handle *weak* coupling between chemical and mechanical fields has been shortly reviewed.

A chemo-mechanics coupled model has been then constructed starting from thermodynamics considerations and, in particular, employing the thermodynamics of irreversible processes.

It has been shown theoretically that the chemical reaction may directly depend on the strain tensor, in particular should be influenced by $\text{tr} \mathbf{E}$ and its spatial gradients.

The classical mechanistic model for oxygen reaction–diffusion independent of mechanical variables [2,3] has been also recovered by introducing simplifying hypotheses, which have been explicitly stated.

In fact, the model presented in this article represents a possible development of the mechanistic scheme taking into account direct and indirect couplings with mechanics.

Work is under progress in order to assess experimentally the fully coupled chemo-mechanics model.

Different tests typologies have been proposed at the end of Section 3. Results from an experimental activity on chemo-mechanics couplings employing EIT measurements in polymer thermo-oxidised resins will be the object of a future communication by the authors.

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