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Citation: Loeffel, Kaspar, and Lallit Anand. "A Chemo-Thermo-Mechanically Coupled Theory for Elastic-viscoplastic Deformation, Diffusion, and Volumetric Swelling Due to a Chemical Reaction." *International Journal of Plasticity* 27, no. 9 (September 2011): 1409-1431.

As Published: <http://dx.doi.org/10.1016/j.ijplas.2011.04.001>

Publisher: Elsevier B.V.

Persistent URL: <http://hdl.handle.net/1721.1/107735>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

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A chemo-thermo-mechanically coupled theory for elastic-viscoplastic deformation, diffusion, and volumetric swelling due to a chemical reaction

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July 26, 2011

Abstract

Thermal barrier coatings (TBCs) are applied to superalloy turbine blades to provide thermal insulation and oxidation protection. A TBC consists of an oxide/metal bilayer: the outer oxide layer (top-coat) imparts thermal insulation, while the metallic layer (bond-coat) affords oxidation protection through the formation of a thermally-grown-oxide (TGO) at elevated temperatures. The TGO layer possesses significantly different elastic, thermal expansion, and creep properties than the surrounding top-coat and bond-coat layers. An intrinsic mechanism which controls the long-term stability and mechanical integrity of a TBC is the volumetric change accompanying the oxide formation, and the attendant locally large stresses that can arise due to the geometrically uneven development of the TGO layer. In this paper we focus on modeling the response of the bond-coat material and its oxidation, and present a new continuum-level thermodynamically-consistent, large-deformation, fully three-dimensional theory which couples high-temperature elastic-viscoplastic deformation of the material with diffusion of oxygen, eventually leading to an oxidation reaction in which the reaction-product causes permanent swelling.

The theory is chemo-thermo-mechanically coupled and complex, and at this point in time the list of material parameters appearing in the theory are not fully known. Once the material parameters in our theory are calibrated from suitable experiments, and the theory is numerically-implemented and validated, then the numerical simulation capability should provide an important ingredient for analyzing the evolution of the local stress and strain states which are important ingredients for the life-prediction and performance-improvement of TBCs.

Keywords: Chemo-thermo-mechanics; Diffusion; Chemical reaction; Viscoplasticity; Thermal barrier coatings

1 Introduction

Turbine inlet temperatures in the gas path of modern high-performance gas turbines operate at $\approx 1400^\circ\text{C}$. In the high-temperature regions of the turbine, special high-melting-point nickel-based superalloy blades and vanes are used, which retain strength and resist oxidation and hot corrosion at extreme temperatures. These superalloys melt at $\approx 1300^\circ\text{C}$, which means that the blades (and vanes) closest to the combustor may be operating in gas-path temperatures which far exceed their melting point, and the blades must therefore be *cooled* to acceptable service temperatures, $\approx 1050^\circ\text{C}$ (a homologous temperature of about ≈ 0.8) in order to maintain integrity. Accordingly, modern turbine blades subjected to the hottest gas flows take the form of

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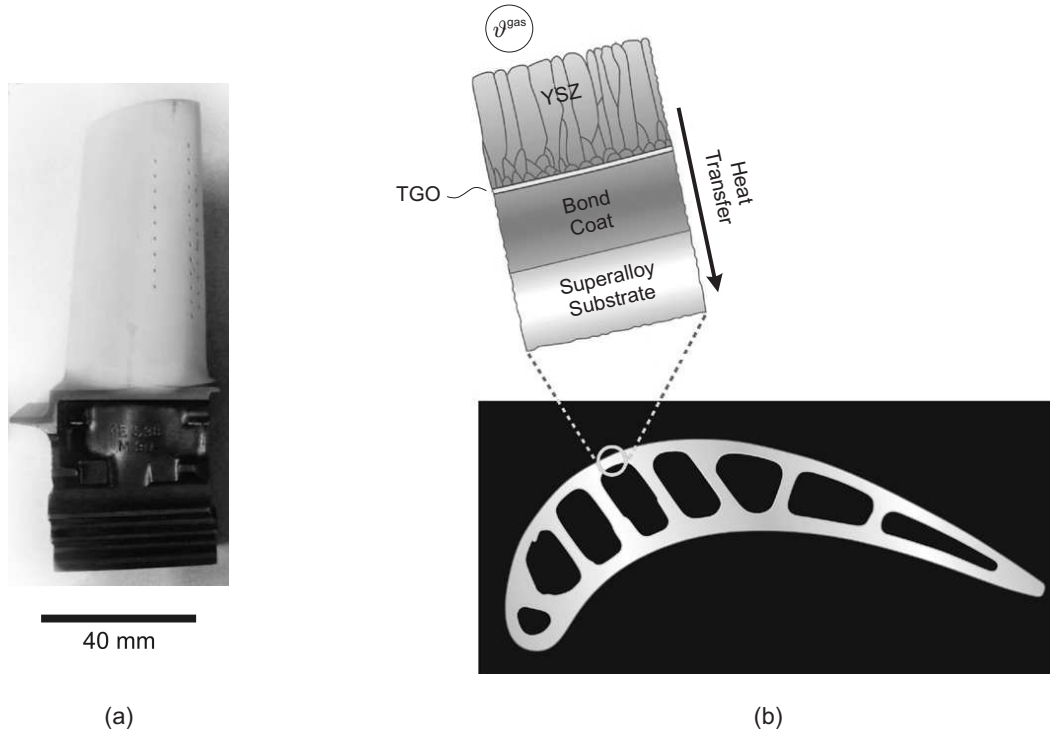


Figure 1: (a) Coated turbine blade (adapted from Besmann, 2009); (b) Schematic of turbine blade cross section with a magnification of the surface region (adapted from Evans et al., 2008).

elaborate single-crystal superalloy investment castings that contain intricate internal passages and surface-hole patterns, which are necessary to channel and direct cooling air within the blade, as well as over its exterior surfaces. After casting, the exposed surface of a high-temperature turbine blade is also typically coated with a *thermal barrier coating* (TBC), approximately $100\text{--}250\mu\text{m}$ thick, which acts as a thermal insulator and oxidation inhibitor, and serves to increase the life of the blade. The current generation of TBCs can accommodate surface temperatures up to $\approx 1275^\circ\text{C}$. A TBC consists of two layers: (a) a metallic layer, or *bond-coat* (BC), deposited on the superalloy — the bond coat is typically an alloy based on Ni(Al) with various additions (such as Cr, Co, Pt, Y, and Hf); and (b) an yttria-stabilized-zirconia (YSZ) *top-coat* deposited on the bond-coat (Feuerstein et al., 2008). The top-coat imparts thermal insulation, while the bond-coat affords oxidation protection through the formation of a second oxide, primarily $\alpha\text{-Al}_2\text{O}_3$, as well as plastic accommodation of misfit strains (Padture et al. 2002; Evans et al., 2008). A coated turbine blade, along with a schematic of the cross section, is shown in Fig. 1.

One of the problems limiting the use of TBCs is their long-term durability. The main intrinsic mechanisms which control the long-term stability and mechanical integrity of a TBC system are (a) the oxidation of the bond-coat; and (b) the time-dependent deformation and degradation processes in the multi-layered system. The exposure of the bond-coat/YSZ interface to high temperatures and high oxygen concentration leads to the development of a thermally-grown $\alpha\text{-Al}_2\text{O}_3$ layer (TGO). When the effects of property mismatch are combined with the volumetric changes associated with the oxide formation, especially when the latter are accompanied by a constrained expansion of the TGO, large local stresses can develop. The location and magnitude of these stresses strongly depend on the thickness and morphology of the TGO layer. Such stresses often lead to the nucleation of microcracks at or near the oxide interfaces. *As emphasized by Evans et al. (2008), it is growth of the TGO layer which is directly responsible for all the intrinsic failure mechanisms of TBCs.* Failure of a TBC system often occurs either by debonding at the TGO/bond-coat interface, or the YSZ/TGO interface (cf., e.g., Sridharan et al., 2004, 2005; Evans et al., 2008).

From a Mechanics and Materials point of view, TBC systems involve complex interplay among numerous phenomena: diffusion, oxidation, coupled thermo-elasto-viscoplastic deformation, and damage. It is difficult

to experimentally isolate and determine the relative effects of all the variables on TBC life, due to the fact that these mechanisms are strongly coupled. Further, the driving forces for these various processes are time-dependent and highly heterogeneous. Thus, to gain an understanding of the local stress/strain/damage conditions responsible for ultimate failure of TBCs requires studies which are underpinned by mechanism-based constitutive models that incorporate time-dependent diffusion, oxidation, elastic-viscoplastic deformation, and realistic interfacial behavior. Although several important contributions to modeling the deformation and failure of TBCs have been reported in the literature in the past decade (cf., e.g., Mumm and Evans, 2000; Busso et al., 2001, 2006, 2009, 2010; Evans et al., 2001; Padture et al., 2002; Karlsson et al., 2002; Xu et al., 2003; Clarke and Levi, 2003; He et al., 2003; Davis and Evans, 2006; Evans and Hutchinson, 2007; Mercer et al., 2008; Evans et al., 2008; and the references to the substantial literature therein), much experimental, theoretical, and computational research still needs to be done to develop a robust and validated simulation capability for elucidating the relative importance of the large variety of coupled phenomena, and their effects on TBC life.

The purpose of this paper is to make a contribution to the broader overall effort that is needed. Specifically, with a focus on modeling the response of the bond-coat material and its oxidation, we present a new continuum-level, thermodynamically-consistent, large-deformation, fully three-dimensional theory which couples high-temperature elastic-viscoplastic deformation of the material with diffusion of oxygen, eventually leading to an oxidation reaction in which the reaction-product causes permanent swelling. The theory is chemo-thermo-mechanically coupled and complex, and at this point in time the list of material parameters appearing in the theory are not fully known. Once the material parameters in our theory are calibrated from suitable experiments, and the theory is numerically-implemented and validated, then the numerical simulation capability should provide an important ingredient for analyzing the evolution of the local stress and strain states which are important ingredients for the life-prediction and performance-improvement of TBCs.

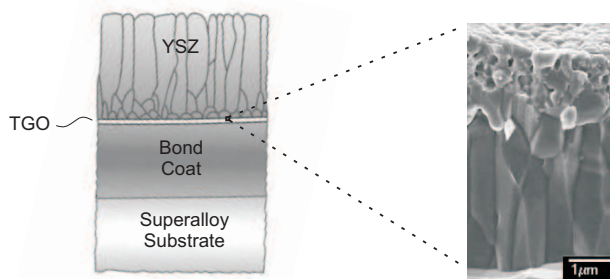


Figure 2: Schematic of TBC system with SEM micrograph of a TGO scale. Inward-growing oxide has columnar structure, while equiaxed grains near the top of the scale are the result of a small amount of outward growth (adapted from Clarke, 2003).

Regarding the mechanism of oxidation in a TBC system, it is important to note that in general, growth of an α - Al_2O_3 scale on an Al-containing alloy may occur by both the inward diffusion of oxygen and the outward diffusion of aluminum through the oxide scale. However, bond-coat alloys invariably contain reactive elements such as yttrium and hafnium, and it has been experimentally observed that the presence of such reactive elements even in a trace amount (a few hundredths or tenths of a percent), can significantly increase the oxidation resistance of the alloy by improving scale adherence and reducing scale growth by *suppressing* the outward diffusion of Al and Cr (cf., e.g., Hou and Stringer, 1995; Yang, 2008). Specifically, in TBCs, the presence of such reactive elements suppresses the outward transport of aluminum, and favors the inward transport of oxygen along the grain boundaries of the thermally-grown oxide — leading to an inward-growing, columnar oxide scale at the TGO-BC interface (cf., e.g., Haynes et al., 1999). A micrograph of a mainly inward-growing oxide scale on a bond-coat alloy, taken from Clarke (2003), is shown in Fig. 2. Based on this experimental observation, in the development of our theory

- *we limit our considerations to the inward diffusion of oxygen anions, and neglect the outward diffusion of aluminum cations.*

As a result, the theory developed here will not be applicable to situations where outward diffusion of metallic cations represents the dominant transport mechanism, which is the case for oxidation of many *pure* metals. However, there are other situations in which the inward diffusion of oxygen is the major transport mechanism. Examples include: (a) Oxidation of silicon (cf. e.g., Rank and Weinert, 1990); and (b) Oxidation of solid-oxide fuel cell (SOFC) interconnects made from reactive element containing Ni(-Fe)-Cr alloys (cf. e.g., Yang, 2008; Saillard et al., 2011). Our theory should be useful in modeling such phenomena.

Finally, we emphasize that the purpose of this paper is only to report on the formulation of the theory. We leave a report concerning its numerical implementation and validation to a future paper.

2 Kinematics

Consider a macroscopically-homogeneous body B with the region of space it occupies in a fixed *reference configuration*, and denote by \mathbf{X} an arbitrary material point of B . A *motion* of B is then a smooth one-to-one mapping $\mathbf{x} = \chi(\mathbf{X}, t)$ with *deformation gradient*, *velocity*, and *velocity gradient* given by¹

$$\mathbf{F} = \nabla \chi, \quad \mathbf{v} = \dot{\chi}, \quad \mathbf{L} = \text{grad } \mathbf{v} = \dot{\mathbf{F}}\mathbf{F}^{-1}. \quad (2.1)$$

Following modern developments of large-deformation plasticity theory (cf., e.g., Anand and Gurtin, 2003; Gurtin and Anand, 2005), we base our theory on the Kröner (1960) – Lee (1969) multiplicative decomposition of the deformation gradient,

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^i. \quad (2.2)$$

As is standard, we assume that

$$J \stackrel{\text{def}}{=} \det \mathbf{F} > 0, \quad (2.3)$$

and hence, using (2.2),

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

so that \mathbf{F}^e and \mathbf{F}^i are invertible. Here, suppressing the argument t :

- (i) $\mathbf{F}^e(\mathbf{X})$ represents the local deformation of material in an infinitesimal neighborhood of \mathbf{X} due to stretch and rotation of the microscopic structure;
- (ii) $\mathbf{F}^i(\mathbf{X})$ represents the local deformation in an infinitesimal neighborhood of material at \mathbf{X} due to the two major micromechanisms for inelastic deformation under consideration: (a) isochoric viscoplastic deformation due to motion of dislocations, and (b) permanent volumetric swelling due to a chemical reaction.

We refer to \mathbf{F}^e and \mathbf{F}^i as the *elastic and inelastic distortions*, and we refer to the local space at \mathbf{X} represented by the range of $\mathbf{F}^i(\mathbf{X})$, as a local *structural space*.²

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

$$\mathbf{F}^e = \mathbf{R}^e \mathbf{U}^e, \quad (2.5)$$

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

$$\mathbf{U}^e = \sqrt{\mathbf{F}^{eT} \mathbf{F}^e}. \quad (2.6)$$

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

²Also sometimes referred to as the *intermediate* local space at \mathbf{X} .

As is standard, we define

$$\mathbf{C}^e = \mathbf{U}^{e2} = \mathbf{F}^{e\top} \mathbf{F}^e. \quad (2.7)$$

By (2.1)₃ and (2.2),

$$\mathbf{L} = \mathbf{L}^e + \mathbf{F}^e \mathbf{L}^i \mathbf{F}^{e-1}, \quad (2.8)$$

with

$$\mathbf{L}^e = \dot{\mathbf{F}}^e \mathbf{F}^{e-1}, \quad \mathbf{L}^i = \dot{\mathbf{F}}^i \mathbf{F}^{i-1}. \quad (2.9)$$

As is standard, we define the elastic and inelastic stretching and spin tensors through

$$\left. \begin{aligned} \mathbf{D}^e &= \text{sym } \mathbf{L}^e, & \mathbf{W}^e &= \text{skw } \mathbf{L}^e, \\ \mathbf{D}^i &= \text{sym } \mathbf{L}^i, & \mathbf{W}^i &= \text{skw } \mathbf{L}^i, \end{aligned} \right\} \quad (2.10)$$

so that $\mathbf{L}^e = \mathbf{D}^e + \mathbf{W}^e$ and $\mathbf{L}^i = \mathbf{D}^i + \mathbf{W}^i$.

We make the following additional kinematical assumptions concerning inelastic flow:

(i) We denote by $\xi(\mathbf{X}, t)$,

$$0 \leq \xi(\mathbf{X}, t) \leq 1,$$

the local *volume fraction of oxide* at \mathbf{X} at time t , and assume that the inelastic stretching \mathbf{D}^i is additively decomposable as

$$\mathbf{D}^i = \mathbf{D}^s + (1 - \omega) \mathbf{D}_{bc}^p + \omega \mathbf{D}_{ox}^p. \quad (2.11)$$

Here, \mathbf{D}^s represents an inelastic stretching resulting from the oxidation reaction, and is given by

$$\mathbf{D}^s = \dot{\xi} \mathbb{S}, \quad \dot{\xi} \geq 0, \quad (2.12)$$

where \mathbb{S} gives the direction and magnitude of the swelling due to the oxidation reaction. Further,

$$\mathbf{D}_{bc}^p \quad \text{with} \quad \text{tr } \mathbf{D}_{bc}^p = 0, \quad (2.13)$$

represents an *incompressible* plastic stretching due to viscoplastic flow of the unoxidized *bond-coat*, while

$$\mathbf{D}_{ox}^p \quad \text{with} \quad \text{tr } \mathbf{D}_{ox}^p = 0, \quad (2.14)$$

represents an *incompressible* plastic stretching due to viscoplastic flow of the *oxide*. Note that a central underlying modeling assumption of our theory is the treatment of “oxidation front” as a *thin transition layer* containing a mixture of oxide and bond-coat with volume fraction $\xi \in [0, 1]$.³ Finally,

$$\omega = \bar{\omega}(\xi) \quad \text{with} \quad \omega \in [0, 1], \quad (2.15)$$

represents a function that characterizes the relative extent of plastic flow in the bond coat and oxide in the “oxidation front.”

(ii) Second, from the outset we constrain the theory by limiting our discussion to circumstances under which the material may be idealized as isotropic (cf. § 7.3). For isotropic elastic-viscoplastic theories utilizing the Kröner decomposition, it is widely assumed that the plastic flow is *irrotational*, in the sense that⁴

$$\mathbf{W}^i = \mathbf{0}. \quad (2.16)$$

Then, trivially, $\mathbf{L}^i \equiv \mathbf{D}^i$ and

$$\dot{\mathbf{F}}^i = \mathbf{D}^i \mathbf{F}^i. \quad (2.17)$$

³Our approach is distinct from the recent approach of Saillard et al. (2010) who consider a *sharp interface theory* for modeling the “oxidation front.”

⁴This assumption is adopted here solely on pragmatic grounds: when discussing finite deformations the theory without plastic spin is far simpler than one with plastic spin.

For later use we define a *scalar plastic flow rate* and the *direction of plastic flow* of the unoxidized bond-coat by

$$d_{bc}^p \stackrel{\text{def}}{=} |\mathbf{D}_{bc}^p| \geq 0, \quad \mathbf{N}_{bc}^p \stackrel{\text{def}}{=} \frac{\mathbf{D}_{bc}^p}{d_{bc}^p} \quad (\text{when } d_{bc}^p > 0), \quad \text{so that} \quad \mathbf{D}_{bc}^p = d_{bc}^p \mathbf{N}_{bc}^p. \quad (2.18)$$

Similarly, we define a *scalar plastic flow rate* and the *direction of plastic flow* of the oxide by

$$d_{ox}^p \stackrel{\text{def}}{=} |\mathbf{D}_{ox}^p| \geq 0, \quad \mathbf{N}_{ox}^p \stackrel{\text{def}}{=} \frac{\mathbf{D}_{ox}^p}{d_{ox}^p} \quad (\text{when } d_{ox}^p > 0), \quad \text{so that} \quad \mathbf{D}_{ox}^p = d_{ox}^p \mathbf{N}_{ox}^p. \quad (2.19)$$

3 Frame-indifference

A *change in frame*, at each *fixed time* t , is a transformation — defined by a rotation $\mathbf{Q}(t)$ and a spatial point $\mathbf{y}(t)$ — which transforms *spatial points* \mathbf{x} to spatial points

$$\mathbf{x}^* = \mathcal{F}(\mathbf{x}), \quad (3.1)$$

$$= \mathbf{y}(t) + \mathbf{Q}(t)(\mathbf{x} - \mathbf{o}), \quad (3.2)$$

with \mathbf{o} a fixed spatial origin, and the function \mathcal{F} represents a rigid mapping of the observed space into itself. By (3.2) the transformation law for the motion $\mathbf{x} = \chi(\mathbf{X}, t)$ has the form

$$\chi^*(\mathbf{X}, t) = \mathbf{y}(t) + \mathbf{Q}(t)(\chi(\mathbf{X}, t) - \mathbf{o}). \quad (3.3)$$

Hence the deformation gradient \mathbf{F} transforms according to

$$\mathbf{F}^* = \mathbf{Q}\mathbf{F}. \quad (3.4)$$

The reference configuration and the intermediate structural space are independent of the choice of such changes in frame; thus

$$\mathbf{F}^i \quad \text{is invariant under a change in frame.} \quad (3.5)$$

This observation, (2.2), and (3.4) yield the transformation law

$$\mathbf{F}^{e*} = \mathbf{Q}\mathbf{F}^e. \quad (3.6)$$

Also, by (2.9)₂

$$\mathbf{L}^i \quad \text{is invariant,} \quad (3.7)$$

and, by (2.9)₁, $\mathbf{L}^{e*} = \mathbf{Q}\mathbf{L}^e\mathbf{Q}^\top + \dot{\mathbf{Q}}\mathbf{Q}^\top$, and hence

$$\mathbf{D}^{e*} = \mathbf{Q}\mathbf{D}^e\mathbf{Q}^\top, \quad \mathbf{W}^{e*} = \mathbf{Q}\mathbf{W}^e\mathbf{Q}^\top + \dot{\mathbf{Q}}\mathbf{Q}^\top. \quad (3.8)$$

Further, by (2.5),

$$\mathbf{F}^{e*} = \mathbf{Q}\mathbf{R}^e\mathbf{U}^e,$$

and we may conclude from the uniqueness of the polar decomposition that

$$\mathbf{R}^{e*} = \mathbf{Q}\mathbf{R}^e, \quad \text{and} \quad \mathbf{U}^e \quad \text{is invariant,} \quad (3.9)$$

and hence also that

$$\mathbf{C}^e \quad \text{is invariant.} \quad (3.10)$$

4 Balance of forces and moments

Throughout, we denote by P an arbitrary *part* (subregion) of the reference body B with \mathbf{n}_R the outward unit normal on the boundary ∂P of P .

Since time scales associated with species diffusion are usually considerably longer than those associated with wave propagation, we neglect all inertial effects. Then standard considerations of balance of forces and moments, when expressed referentially, give:

- (a) There exists a stress tensor \mathbf{T}_R , called the Piola stress, such that the surface traction on an element of the surface ∂P of P , is given by

$$\mathbf{t}_R(\mathbf{n}_R) = \mathbf{T}_R \mathbf{n}_R. \quad (4.1)$$

- (b) \mathbf{T}_R satisfies the macroscopic force balance

$$\text{Div } \mathbf{T}_R + \mathbf{b}_R = \mathbf{0}, \quad (4.2)$$

where \mathbf{b}_R is an external body force per unit reference volume, which, consistent with neglect of inertial effects, is taken to be time-independent.

- (c) \mathbf{T}_R obeys the symmetry condition

$$\mathbf{T}_R \mathbf{F}^\top = \mathbf{F} \mathbf{T}_R^\top, \quad (4.3)$$

which represents a balance of moments.

Further, under a change in frame \mathbf{T}_R transforms as

$$\mathbf{T}_R^* = \mathbf{Q} \mathbf{T}_R. \quad (4.4)$$

Finally, as is standard, the Piola stress \mathbf{T}_R is related to the standard symmetric Cauchy stress \mathbf{T} in the deformed body by

$$\mathbf{T}_R = J \mathbf{T} \mathbf{F}^{-\top}, \quad (4.5)$$

so that

$$\mathbf{T} = J^{-1} \mathbf{T}_R \mathbf{F}^\top; \quad (4.6)$$

and, as is also standard, under a change in frame \mathbf{T} transforms as

$$\mathbf{T}^* = \mathbf{Q} \mathbf{T} \mathbf{Q}^\top. \quad (4.7)$$

5 Balance law for the diffusing species

As discussed in the Introduction, the presence of small amounts of reactive elements such as yttrium and hafnium in the bond coat suppresses the outward transport of aluminum, and favors the inward transport of oxygen along the grain boundaries of the thermally-grown oxide — leading to an inward-growing, columnar oxide scale at the TGO-BC interface. Based on this experimental observation, in the development of our theory *we limit our considerations to the diffusion of single species — oxygen.*

Let

$$c_R(\mathbf{X}, t) \quad (5.1)$$

denote the *total number of moles of diffusing species (that is, oxygen) per unit reference volume* which can cause a chemical reaction. Note that the quantity c_R includes the amount of moles of diffusing species that have already undergone the chemical reaction.

Changes in the number of moles of diffusing species in P are brought about by the diffusion across the boundary ∂P , which is characterized by a *flux* $\mathbf{j}_R(\mathbf{X}, t)$, the number of moles of diffusing species measured per unit area per unit time, so that

$$- \int_{\partial P} \mathbf{j}_R \cdot \mathbf{n}_R \, da_R$$

represents the number of moles of diffusing species entering P across ∂P per unit time. The *balance law for the diffusing species* therefore takes the form

$$\overline{\int_P \dot{c}_R dv_R} = - \int_{\partial P} \mathbf{j}_R \cdot \mathbf{n}_R da_R, \quad (5.2)$$

for every part P. Bringing the time derivative in (5.2) inside the integral and using the divergence theorem on the integral over ∂P , we find that

$$\int_P (\dot{c}_R + \text{Div} \mathbf{j}_R) dv_R = 0. \quad (5.3)$$

Since P is arbitrary, this leads to the following local balance:

$$\dot{c}_R = -\text{Div} \mathbf{j}_R. \quad (5.4)$$

6 Balance of energy. Entropy imbalance

Our discussion of thermodynamics follows Gurtin et al. (2010, § 64) and involves the following fields:

- ε_R the internal energy density per unit reference volume,
- η_R the entropy density per unit reference volume,
- \mathbf{q}_R the heat flux per unit reference area,
- q_R the external heat supply per unit reference volume,
- ϑ the absolute temperature ($\vartheta > 0$),
- μ the chemical potential.

Consider a material region P. Then, consistent with our omission of inertial effects, we neglect kinetic energy, and take the balance law for energy as

$$\overline{\int_P \dot{\varepsilon}_R dv_R} = \int_{\partial P} (\mathbf{T}_R \mathbf{n}_R) \cdot \dot{\boldsymbol{\chi}} da_R + \int_P \mathbf{b}_R \cdot \dot{\boldsymbol{\chi}} dv_R - \int_{\partial P} \mathbf{q}_R \cdot \mathbf{n}_R da_R + \int_P q_R dv_R - \int_{\partial P} \mu \mathbf{j}_R \cdot \mathbf{n}_R da_R, \quad (6.1)$$

where the last term in (6.1) represents the flux of energy carried into P by the flux \mathbf{j}_R of diffusing species. Applying the divergence theorem to the terms in (6.1) involving integrals over the boundary ∂P of P, we obtain

$$\int_P \left(\dot{\varepsilon}_R - (\text{Div} \mathbf{T}_R + \mathbf{b}_R) \cdot \dot{\boldsymbol{\chi}} - \mathbf{T}_R : \dot{\mathbf{F}} + \text{Div} \mathbf{q}_R - q_R + \mu \text{Div} \mathbf{j}_R + \mathbf{j}_R \cdot \nabla \mu \right) dv_R = 0, \quad (6.2)$$

which upon use of the balance laws (4.2) and (5.4), and using the fact that (6.2) must hold for all parts P, gives the local form of the energy balance as

$$\dot{\varepsilon}_R = \mathbf{T}_R : \dot{\mathbf{F}} + \mu \dot{c}_R - \text{Div} \mathbf{q}_R + q_R - \mathbf{j}_R \cdot \nabla \mu. \quad (6.3)$$

Also, the second law takes the form of an entropy imbalance

$$\overline{\int_P \dot{\eta}_R dv_R} \geq - \int_{\partial P} \frac{\mathbf{q}_R \cdot \mathbf{n}_R}{\vartheta} da_R + \int_P \frac{q_R}{\vartheta} dv_R, \quad (6.4)$$

in which case the local entropy imbalance has the form

$$\dot{\eta}_R \geq -\text{Div} \left(\frac{\mathbf{q}_R}{\vartheta} \right) + \frac{q_R}{\vartheta}. \quad (6.5)$$

Then, in view of the local energy balance (6.3),

$$\begin{aligned} -\text{Div}\left(\frac{\mathbf{q}_R}{\vartheta}\right) + \frac{q_R}{\vartheta} &= \frac{1}{\vartheta}(-\text{Div}\mathbf{q}_R + q_R) + \frac{1}{\vartheta^2}\mathbf{q}_R \cdot \nabla\vartheta, \\ &= \frac{1}{\vartheta}\left(\dot{\varepsilon}_R - \mathbf{T}_R : \dot{\mathbf{F}} - \mu\dot{c}_R + \frac{1}{\vartheta}\mathbf{q}_R \cdot \nabla\vartheta + \mathbf{j}_R \cdot \nabla\mu\right), \end{aligned}$$

and this with the local entropy imbalance (6.5) implies that

$$(\dot{\varepsilon}_R - \vartheta\dot{\eta}_R) - \mathbf{T}_R : \dot{\mathbf{F}} - \mu\dot{c}_R + \frac{1}{\vartheta}\mathbf{q}_R \cdot \nabla\vartheta + \mathbf{j}_R \cdot \nabla\mu \leq 0. \quad (6.6)$$

Introducing the Helmholtz free energy

$$\psi_R = \varepsilon_R - \vartheta\eta_R, \quad (6.7)$$

(6.6) yields the following local free-energy imbalance

$$\dot{\psi}_R + \eta_R\dot{\vartheta} - \mathbf{T}_R : \dot{\mathbf{F}} - \mu\dot{c}_R + \frac{1}{\vartheta}\mathbf{q}_R \cdot \nabla\vartheta + \mathbf{j}_R \cdot \nabla\mu \leq 0. \quad (6.8)$$

6.1 Stress-power

The term $\mathbf{T}_R : \dot{\mathbf{F}}$ represents the stress-power per unit reference volume. Using (2.2), (4.5), and (2.9)₂ the stress-power may be written as

$$\begin{aligned} \mathbf{T}_R : \dot{\mathbf{F}} &= \mathbf{T}_R : (\dot{\mathbf{F}}^e \mathbf{F}^i + \mathbf{F}^e \dot{\mathbf{F}}^i), \\ &= (\mathbf{T}_R \mathbf{F}^{i\top}) : \dot{\mathbf{F}}^e + (\mathbf{F}^{e\top} \mathbf{T}_R) : \dot{\mathbf{F}}^i, \\ &= (J\mathbf{F}^{e-1} \mathbf{T} \mathbf{F}^{e-\top}) : (\mathbf{F}^{e\top} \dot{\mathbf{F}}^e) + (\mathbf{C}^e J\mathbf{F}^{e-1} \mathbf{T} \mathbf{F}^{e-\top}) : \mathbf{L}^i. \end{aligned} \quad (6.9)$$

In view of (6.9), we introduce two new stress measures:

- The elastic second Piola stress,

$$\mathbf{T}^e \stackrel{\text{def}}{=} J\mathbf{F}^{e-1} \mathbf{T} \mathbf{F}^{e-\top}, \quad (6.10)$$

which is *symmetric* on account of the symmetry of the Cauchy stress \mathbf{T} .

- The Mandel stress,

$$\mathbf{M}^e \stackrel{\text{def}}{=} \mathbf{C}^e \mathbf{T}^e, \quad (6.11)$$

which in general is *not symmetric*.

Note that on account of the transformation rule (3.6) for \mathbf{F}^e , and the transformation rule (4.7), the elastic second Piola stress and the Mandel stress are invariant under a change in frame,

$$\mathbf{T}^{e*} = \mathbf{T}^e \quad \text{and} \quad \mathbf{M}^{e*} = \mathbf{M}^e. \quad (6.12)$$

Further, from (2.7)

$$\dot{\mathbf{C}}^e = \dot{\mathbf{F}}^{e\top} \mathbf{F}^e + \mathbf{F}^{e\top} \dot{\mathbf{F}}^e. \quad (6.13)$$

Thus, using the definitions (6.10), (6.11) and the relation (6.13), the stress-power (6.9) may be written as

$$\mathbf{T}_R : \dot{\mathbf{F}} = \underbrace{\frac{1}{2}\mathbf{T}^e : \dot{\mathbf{C}}^e}_{\text{elastic power}} + \underbrace{\mathbf{M}^e : \mathbf{L}^i}_{\text{inelastic power}}. \quad (6.14)$$

Further, use of the assumptions (2.11), (2.12), (2.13), (2.14), and (2.16) concerning plastic flow gives

$$\mathbf{T}_R : \dot{\mathbf{F}} = \frac{1}{2}\mathbf{T}^e : \dot{\mathbf{C}}^e + (1 - \omega)\mathbf{M}_0^e : \mathbf{D}_{bc}^p + \omega\mathbf{M}_0^e : \mathbf{D}_{ox}^p + \dot{\xi}\mathbf{M}^e : \mathbb{S}. \quad (6.15)$$

Using (6.15) in (6.8) allows us to write the free energy imbalance as

$$\dot{\psi}_R + \eta_R\dot{\vartheta} - \frac{1}{2}\mathbf{T}^e : \dot{\mathbf{C}}^e - (1 - \omega)\mathbf{M}_0^e : \mathbf{D}_{bc}^p - \omega\mathbf{M}_0^e : \mathbf{D}_{ox}^p - \dot{\xi}\mathbf{M}^e : \mathbb{S} - \mu\dot{c}_R + \frac{1}{\vartheta}\mathbf{q}_R \cdot \nabla\vartheta + \mathbf{j}_R \cdot \nabla\mu \leq 0. \quad (6.16)$$

Finally, note that $\psi_{\mathbf{R}}$, $\eta_{\mathbf{R}}$, ϑ , ξ , and $c_{\mathbf{R}}$ are invariant under a change in frame since they are scalar fields, and on account of the transformation rules discussed in § 3, and the transformation rules (6.12), the fields

$$\mathbf{C}^e, \quad \mathbf{D}_{\text{bc}}^p, \quad \mathbf{D}_{\text{ox}}^p, \quad \mathbb{S}, \quad \mathbf{T}^e, \quad \text{and} \quad \mathbf{M}^e, \quad (6.17)$$

are also invariant, as are the fields

$$\mathbf{q}_{\mathbf{R}}, \quad \nabla\vartheta, \quad \mathbf{j}_{\mathbf{R}}, \quad \text{and} \quad \nabla\mu, \quad (6.18)$$

since they are referential vector fields.

7 Constitutive theory

7.1 Basic constitutive equations

Next, guided by the free-energy imbalance (6.16), we first consider the following set of constitutive equations for the free energy $\psi_{\mathbf{R}}$, the stress \mathbf{T}^e , the entropy $\eta_{\mathbf{R}}$, and the chemical potential μ :

$$\left. \begin{aligned} \psi_{\mathbf{R}} &= \bar{\psi}_{\mathbf{R}}(\mathbf{\Lambda}), \\ \mathbf{T}^e &= \bar{\mathbf{T}}^e(\mathbf{\Lambda}), \\ \eta_{\mathbf{R}} &= \bar{\eta}_{\mathbf{R}}(\mathbf{\Lambda}), \\ \mu &= \bar{\mu}(\mathbf{\Lambda}), \end{aligned} \right\} \quad (7.1)$$

where $\mathbf{\Lambda}$ denotes the list

$$\mathbf{\Lambda} = (\mathbf{C}^e, \vartheta, c_{\mathbf{R}}, \xi). \quad (7.2)$$

Substituting the constitutive equations (7.1) into the dissipation inequality, we find that the free-energy imbalance (6.16) may then be written as

$$\begin{aligned} & \left(\frac{\partial \bar{\psi}_{\mathbf{R}}}{\partial \mathbf{E}^e} - \frac{1}{2} \bar{\mathbf{T}}^e \right) : \dot{\mathbf{C}}^e + \left(\frac{\partial \bar{\psi}_{\mathbf{R}}}{\partial \vartheta} + \bar{\eta}_{\mathbf{R}} \right) \dot{\vartheta} + \left(\frac{\partial \bar{\psi}_{\mathbf{R}}}{\partial c_{\mathbf{R}}} - \bar{\mu} \right) \dot{c}_{\mathbf{R}} \\ & - (1 - \omega) \mathbf{M}_0^e : \mathbf{D}_{\text{bc}}^p - \omega \mathbf{M}_0^e : \mathbf{D}_{\text{ox}}^p - \left(\mathbf{M}^e : \mathbb{S} - \frac{\partial \bar{\psi}_{\mathbf{R}}}{\partial \xi} \right) \dot{\xi} + \frac{1}{\vartheta} \mathbf{q}_{\mathbf{R}} \cdot \nabla\vartheta + \mathbf{j}_{\mathbf{R}} \cdot \nabla\bar{\mu} \leq 0. \end{aligned} \quad (7.3)$$

This inequality is to hold for all values of $\mathbf{\Lambda}$. Since $\dot{\mathbf{C}}^e$, $\dot{\vartheta}$ and $\dot{c}_{\mathbf{R}}$ appear linearly, their ‘‘coefficients’’ must vanish, for otherwise $\dot{\mathbf{C}}^e$, $\dot{\vartheta}$, and $\dot{c}_{\mathbf{R}}$ may be chosen to violate (7.3). We are therefore led to the thermodynamic restriction that the free energy determines the stress \mathbf{T}^e , the entropy η , and the chemical potential μ through the ‘‘state relations’’

$$\left. \begin{aligned} \mathbf{T}^e &= 2 \frac{\partial \bar{\psi}_{\mathbf{R}}(\mathbf{\Lambda})}{\partial \mathbf{C}^e}, \\ \eta_{\mathbf{R}} &= - \frac{\partial \bar{\psi}_{\mathbf{R}}(\mathbf{\Lambda})}{\partial \vartheta}, \\ \mu &= \frac{\partial \bar{\psi}_{\mathbf{R}}(\mathbf{\Lambda})}{\partial c_{\mathbf{R}}}. \end{aligned} \right\} \quad (7.4)$$

We are then left with the following reduced dissipation inequality

$$(1 - \omega) \mathbf{M}_0^e : \mathbf{D}_{\text{bc}}^p + \omega \mathbf{M}_0^e : \mathbf{D}_{\text{ox}}^p + \mathcal{F} \dot{\xi} - \frac{1}{\vartheta} \mathbf{q}_{\mathbf{R}} \cdot \nabla\vartheta - \mathbf{j}_{\mathbf{R}} \cdot \nabla\mu \geq 0, \quad (7.5)$$

where

$$\mathcal{F} \stackrel{\text{def}}{=} \mathcal{A} + \mathbf{M}^e : \mathbb{S} \quad (7.6)$$

represents a *dissipative* thermodynamic force conjugate to the oxide volume fraction ξ , with

$$\mathcal{A}(\mathbf{\Lambda}) \stackrel{\text{def}}{=} - \frac{\partial \bar{\psi}_{\mathbf{R}}(\mathbf{\Lambda})}{\partial \xi}, \quad (7.7)$$

an energetic constitutive response function, which we call the *affinity* of the chemical reaction; as we shall see, the dissipative force \mathcal{F} plays a fundamental role in the theory.

Henceforth, for brevity and whenever convenient, we write

$$\mathbf{D}_\alpha^p, \quad \alpha = 1, 2, \quad (7.8)$$

with the understanding that

$$\mathbf{D}_1^p \equiv \mathbf{D}_{bc}^p, \quad \text{and} \quad \mathbf{D}_2^p \equiv \mathbf{D}_{ox}^p. \quad (7.9)$$

Also, to account for the strain-hardening characteristics typically observed during plastic deformation, we introduce a pair of scalar *hardening variables*

$$S_\alpha, \quad \alpha = 1, 2, \quad (7.10)$$

to represent important aspects of the microstructural resistance to plastic flow. Since S_α are scalar fields, they are invariant under a change in frame. Then, guided by (7.5), and experience with plasticity theories we assume that

$$\left. \begin{aligned} \mathbf{D}_\alpha^p &= \bar{\mathbf{D}}_\alpha^p(\mathbf{M}_0^e, \vartheta, S_\alpha), \\ \dot{S}_\alpha &= h_\alpha(\mathbf{D}_\alpha^p, \vartheta, S_\alpha), \\ \mathbb{S} &= \bar{\mathbb{S}}(\mathbf{M}^e, \vartheta), \\ \dot{\xi} &= \bar{\xi}(\mathcal{F}, \vartheta, \xi). \end{aligned} \right\} \quad (7.11)$$

To the constitutive equations (7.1) and (7.11), we append a Fourier-type relation for the heat flux, and a Fick-type relation for the flux of the diffusing species,

$$\left. \begin{aligned} \mathbf{q}_R &= -\mathbf{K}(\boldsymbol{\Lambda}) \nabla \vartheta, \\ \mathbf{j}_R &= -\mathbf{M}(\boldsymbol{\Lambda}) \nabla \mu, \end{aligned} \right\} \quad (7.12)$$

where \mathbf{K} is a *thermal conductivity tensor*, and \mathbf{M} is a *mobility tensor*.

Using (7.11), (7.12), (2.18) and (2.19), the dissipation inequality (7.5) may be written as

$$(1 - \omega)(\mathbf{M}_0^e : \bar{\mathbf{N}}_{bc}^p) \bar{d}_{bc}^p + \omega(\mathbf{M}_0^e : \bar{\mathbf{N}}_{ox}^p) \bar{d}_{ox}^p + \mathcal{F} \bar{\xi} + \frac{1}{\vartheta} \nabla \vartheta \cdot \mathbf{K} \nabla \vartheta + \nabla \mu \cdot \mathbf{M} \nabla \mu \geq 0. \quad (7.13)$$

Henceforth, we write

$$\bar{\tau}_\alpha \stackrel{\text{def}}{=} \mathbf{M}_0^e : \bar{\mathbf{N}}_\alpha^p \quad (7.14)$$

for the Mandel stress resolved in the direction of the plastic flow. We also assume that the material is *strongly dissipative* in the sense that

$$\bar{\tau}_\alpha d_\alpha^p > 0 \quad \text{for} \quad d_\alpha^p > 0, \quad (7.15)$$

$$\mathcal{F} \dot{\xi} > 0 \quad \text{for} \quad \dot{\xi} \neq 0, \quad (7.16)$$

$$\nabla \vartheta \cdot \mathbf{K}(\boldsymbol{\Lambda}) \nabla \vartheta > 0 \quad \text{for} \quad \nabla \vartheta \neq \mathbf{0}, \quad (7.17)$$

$$\nabla \mu \cdot \mathbf{M}(\boldsymbol{\Lambda}) \nabla \mu > 0 \quad \text{for} \quad \nabla \mu \neq \mathbf{0}. \quad (7.18)$$

Thus note that the thermal conductivity tensor \mathbf{K} and the mobility tensor \mathbf{M} are positive-definite.

Note that on account of the transformation rules listed in the paragraph containing (6.17) and (6.18), *the constitutive equations (7.1), (7.11), and (7.12) are frame-indifferent.*

7.2 Further consequences of thermodynamics

In view of (7.1), (7.4) and (7.7), we have the *first Gibbs relation*,

$$\dot{\psi}_R = \frac{1}{2} \mathbf{T}^e : \dot{\mathbf{C}}^e - \eta_R \dot{\vartheta} + \mu \dot{c}_R - \mathcal{A} \dot{\xi}, \quad (7.19)$$

which, with (6.7), yields the *second Gibbs relation*

$$\dot{\varepsilon}_R = \vartheta \dot{\eta}_R + \frac{1}{2} \mathbf{T}^e : \dot{\mathbf{C}}^e + \mu \dot{c}_R - \mathcal{A} \dot{\xi}. \quad (7.20)$$

Using balance of energy (6.3), the stress-power relation (6.15), the second Gibbs relation (7.20), the constitutive equations (7.1)_{2,3} and (7.11), and equations (7.15) through (7.18) we arrive at the *entropy balance*

$$\vartheta \dot{\eta}_R = -\text{Div} \mathbf{q}_R + q_R + (1 - \omega) \bar{\tau}_{bc} d_{bc}^p + \omega \bar{\tau}_{ox} d_{ox}^p + \mathcal{F} \dot{\xi} + \nabla \mu \cdot \mathbf{M} \nabla \mu. \quad (7.21)$$

Granted the thermodynamically restricted constitutive relations (7.4), this balance is equivalent to the balance of energy.

Next, the internal energy density is given by

$$\varepsilon_R = \bar{\varepsilon}_R(\mathbf{\Lambda}) \stackrel{\text{def}}{=} \bar{\psi}_R(\mathbf{\Lambda}) + \vartheta \bar{\eta}_R(\mathbf{\Lambda}), \quad (7.22)$$

and, as is standard, the *specific heat* is defined by

$$c \stackrel{\text{def}}{=} \frac{\partial \bar{\varepsilon}(\mathbf{\Lambda})}{\partial \vartheta}. \quad (7.23)$$

Hence, from (7.22)

$$c = \left(\frac{\partial \bar{\psi}(\mathbf{\Lambda})}{\partial \vartheta} + \bar{\eta}(\mathbf{\Lambda}) + \vartheta \frac{\partial \bar{\eta}(\mathbf{\Lambda})}{\partial \vartheta} \right), \quad (7.24)$$

and use of (7.4) gives

$$c = -\vartheta \frac{\partial^2 \bar{\psi}(\mathbf{\Lambda})}{\partial \vartheta^2}. \quad (7.25)$$

Next, from (7.4), (7.7), and (7.25),

$$\begin{aligned} \vartheta \dot{\eta}_R &= -\vartheta \frac{\partial^2 \bar{\psi}(\mathbf{\Lambda})}{\partial \vartheta \partial \mathbf{C}^e} : \dot{\mathbf{C}}^e + c \dot{\vartheta} - \vartheta \frac{\partial^2 \bar{\psi}(\mathbf{\Lambda})}{\partial \vartheta \partial c_R} \dot{c}_R - \vartheta \frac{\partial^2 \bar{\psi}(\mathbf{\Lambda})}{\partial \vartheta \partial \xi} \dot{\xi} \\ &= -\frac{1}{2} \vartheta \frac{\partial \mathbf{T}^e}{\partial \vartheta} : \dot{\mathbf{C}}^e + c \dot{\vartheta} - \vartheta \frac{\partial \mu}{\partial \vartheta} \dot{c}_R + \vartheta \frac{\partial \mathcal{A}}{\partial \vartheta} \dot{\xi}, \end{aligned} \quad (7.26)$$

Then, using (7.25) and (7.26) in (7.21) gives the following partial differential equation for the temperature

$$c \dot{\vartheta} = -\text{Div} \mathbf{q}_R + q_R + (1 - \omega) \bar{\tau}_{bc} d_{bc}^p + \omega \bar{\tau}_{ox} d_{ox}^p + \mathcal{F} \dot{\xi} + \nabla \mu \cdot \mathbf{M} \nabla \mu + \frac{1}{2} \vartheta \frac{\partial \mathbf{T}^e}{\partial \vartheta} : \dot{\mathbf{C}}^e + \vartheta \frac{\partial \mu}{\partial \vartheta} \dot{c}_R - \vartheta \frac{\partial \mathcal{A}}{\partial \vartheta} \dot{\xi}. \quad (7.27)$$

7.3 Isotropy

The following definitions help to make precise our notion of an isotropic material (cf., Anand and Gurtin, 2003):

- (i) Orth^+ = the group of all rotations (the proper orthogonal group);
- (ii) the *symmetry group* \mathcal{G}_R , is the group of all rotations of the *reference* configuration that leaves the response of the material unaltered;
- (iii) the *symmetry group* \mathcal{G}_I at each time t , is the group of all rotations of the *intermediate* structural space that leaves the response of the material unaltered.

We now discuss the manner in which the basic fields transform under such transformations, granted the physically natural requirement of invariance of the stress-power (6.15), or equivalently, the requirement that

$$\mathbf{T}^e : \dot{\mathbf{C}}^e, \quad \mathbf{M}^e : \mathbb{S}, \quad \text{and} \quad \mathbf{M}_0^e : \mathbf{D}_\alpha^p \quad \text{be invariant.} \quad (7.28)$$

7.3.1 Isotropy of the reference configuration

Let \mathbf{Q} be a *time-independent rotation of the reference configuration*. Then $\mathbf{F} \rightarrow \mathbf{F}\mathbf{Q}$, and hence

$$\mathbf{F}^i \rightarrow \mathbf{F}^i\mathbf{Q}, \quad \text{and} \quad \mathbf{F}^e \text{ is invariant, and hence } \mathbf{C}^e \text{ is invariant,} \quad (7.29)$$

so that, by (2.9) and (2.11),

$$\dot{\mathbf{C}}^e, \mathbf{D}_\alpha^p, \text{ and } \mathbb{S} \text{ are invariant.}$$

We may therefore use (7.28) to conclude that

$$\mathbf{T}^e \text{ and } \mathbf{M}^e \text{ are invariant.} \quad (7.30)$$

Thus

- the constitutive equations (7.1) and (7.11) are unaffected by such rotations of the reference configuration.

Turning our attention next to the constitutive equation (7.12)₁ for the heat flux, a standard result from the theory of finite thermoelasticity is that under a symmetry transformation \mathbf{Q} for the reference configuration, the temperature gradient $\nabla\vartheta$ and the heat flux \mathbf{q}_R transform as (cf. Gurtin et al. (2010), § 57.8)

$$\nabla\vartheta \rightarrow \mathbf{Q}^\top \nabla\vartheta, \quad \mathbf{q}_R \rightarrow \mathbf{Q}^\top \mathbf{q}_R.$$

Hence, from (7.11)₁ the thermal conductivity tensor \mathbf{K} must obey

$$\mathbf{K}(\mathbf{\Lambda}) = \mathbf{Q}^\top \mathbf{K}(\mathbf{\Lambda}) \mathbf{Q} \quad \text{for all rotations } \mathbf{Q} \in \mathcal{G}_R. \quad (7.31)$$

By an analogous argument, the mobility tensor \mathbf{M} must obey

$$\mathbf{M}(\mathbf{\Lambda}) = \mathbf{Q}^\top \mathbf{M}(\mathbf{\Lambda}) \mathbf{Q} \quad \text{for all rotations } \mathbf{Q} \in \mathcal{G}_R. \quad (7.32)$$

We refer to the material as *initially isotropic* (and to the reference configuration as undistorted) if

$$\mathcal{G}_R = \text{Orth}^+ \quad (7.33)$$

so that the response of the material is invariant under arbitrary rotations of the reference space. Henceforth

- *we restrict attention to materials that are initially isotropic.*

In this case, the thermal conductivity and the mobility tensors have the representations

$$\mathbf{K}(\mathbf{\Lambda}) = \kappa(\mathbf{\Lambda})\mathbf{1}, \quad \text{with} \quad \kappa(\mathbf{\Lambda}) > 0 \quad (7.34)$$

a scalar thermal conductivity, and

$$\mathbf{M}(\mathbf{\Lambda}) = m(\mathbf{\Lambda})\mathbf{1}, \quad \text{with} \quad m(\mathbf{\Lambda}) > 0 \quad (7.35)$$

a scalar mobility.

7.3.2 Isotropy of the intermediate structural space

Next, let \mathbf{Q} , a *time-independent rotation of the intermediate space*, be a symmetry transformation. Then \mathbf{F} is unaltered by such a rotation, and hence

$$\mathbf{F}^e \rightarrow \mathbf{F}^e\mathbf{Q} \quad \text{and} \quad \mathbf{F}^i \rightarrow \mathbf{Q}^\top \mathbf{F}^i, \quad (7.36)$$

and also

$$\mathbf{C}^e \rightarrow \mathbf{Q}^\top \mathbf{C}^e \mathbf{Q}, \quad \dot{\mathbf{C}}^e \rightarrow \mathbf{Q}^\top \dot{\mathbf{C}}^e \mathbf{Q}, \quad \mathbf{D}_\alpha^p \rightarrow \mathbf{Q}^\top \mathbf{D}_\alpha^p \mathbf{Q}, \quad \mathbb{S} \rightarrow \mathbf{Q}^\top \mathbb{S} \mathbf{Q}. \quad (7.37)$$

Then (7.37) and (7.28) yield the transformation laws

$$\mathbf{T}^e \rightarrow \mathbf{Q}^\top \mathbf{T}^e \mathbf{Q}, \quad \mathbf{M}^e \rightarrow \mathbf{Q}^\top \mathbf{M}^e \mathbf{Q}. \quad (7.38)$$

Thus, with reference to the constitutive equations (7.1) and (7.11), together with (7.34) and (7.35) we conclude that

$$\left. \begin{aligned} \bar{\psi}_R(\mathbf{\Lambda}) &= \bar{\psi}_R(\mathbf{Q}^\top \mathbf{\Lambda} \mathbf{Q}), \\ \mathbf{Q}^\top \bar{\mathbf{T}}^e(\mathbf{\Lambda}) \mathbf{Q} &= \bar{\mathbf{T}}^e(\mathbf{Q}^\top \mathbf{\Lambda} \mathbf{Q}), \\ \bar{\eta}_R(\mathbf{\Lambda}) &= \bar{\eta}_R(\mathbf{Q}^\top \mathbf{\Lambda} \mathbf{Q}), \\ \bar{\mu}(\mathbf{\Lambda}) &= \bar{\mu}(\mathbf{Q}^\top \mathbf{\Lambda} \mathbf{Q}), \\ \mathbf{Q}^\top \bar{\mathbf{D}}_\alpha^p(\mathbf{M}_0^e, \vartheta, S_\alpha) \mathbf{Q} &= \bar{\mathbf{D}}_\alpha^p(\mathbf{Q}^\top \mathbf{M}_0^e \mathbf{Q}, \vartheta, S_\alpha), \\ \mathbf{Q}^\top \bar{\mathbf{S}}(\mathbf{M}^e, \vartheta) \mathbf{Q} &= \bar{\mathbf{S}}(\mathbf{Q}^\top \mathbf{M}^e \mathbf{Q}, \vartheta), \\ h_\alpha(\mathbf{D}^p, \vartheta, S_\alpha) &= h_\alpha(\mathbf{Q}^\top \mathbf{D}^p \mathbf{Q}, \vartheta, S_\alpha), \\ \kappa(\mathbf{\Lambda}) &= \kappa(\mathbf{Q}^\top \mathbf{\Lambda} \mathbf{Q}), \\ m(\mathbf{\Lambda}) &= m(\mathbf{Q}^\top \mathbf{\Lambda} \mathbf{Q}), \end{aligned} \right\} \quad (7.39)$$

with

$$\mathbf{Q}^\top \mathbf{\Lambda} \mathbf{Q} = (\mathbf{Q}^\top \mathbf{C}^e \mathbf{Q}, \vartheta, c_R, \xi),$$

must hold for all rotations \mathbf{Q} in the *symmetry group* \mathcal{G}_I at each time t .

We refer to the material as one which is *continually isotropic*, if in addition to the referential isotropy discussed in the previous subsection,

$$\mathcal{G}_I = \text{Orth}^+, \quad (7.40)$$

so that the response of the material is also invariant under arbitrary rotations of the intermediate space at each time t . Henceforth

- we restrict attention to materials that are not only initially, but also continually isotropic.

In this case,

(‡) the response functions $\bar{\psi}_R$, $\bar{\mathbf{T}}^e$, $\bar{\eta}_R$, $\bar{\mu}$, $\bar{\mathbf{D}}_\alpha^p$, $\bar{\mathbf{S}}$, h_α , κ , and m must also each be *isotropic*.

7.4 Isotropic free energy

An immediate consequence of the isotropy of the free energy is that the free energy function has the representation

$$\bar{\psi}_R(\mathbf{C}^e, \vartheta, c_R, \xi) = \tilde{\psi}_R(\mathcal{I}_{\mathbf{C}^e}, \vartheta, c_R, \xi), \quad (7.41)$$

where

$$\mathcal{I}_{\mathbf{C}^e} = \left(I_1(\mathbf{C}^e), I_2(\mathbf{C}^e), I_3(\mathbf{C}^e) \right)$$

is the list of principal invariants of \mathbf{C}^e . Thus, from (7.4)₁, it follows that

$$\mathbf{T}^e = \bar{\mathbf{T}}^e(\mathcal{I}_{\mathbf{C}^e}, \vartheta, c_R, \xi) = 2 \frac{\partial \tilde{\psi}(\mathcal{I}_{\mathbf{C}^e}, \vartheta, c_R, \xi)}{\partial \mathbf{C}^e}, \quad (7.42)$$

and that $\bar{\mathbf{T}}^e$ is an *isotropic function of* \mathbf{C}^e . Then since the Mandel stress is defined by (cf. (6.11))

$$\mathbf{M}^e = \mathbf{C}^e \mathbf{T}^e,$$

we find that \mathbf{T}^e and \mathbf{C}^e commute,

$$\mathbf{C}^e \mathbf{T}^e = \mathbf{T}^e \mathbf{C}^e, \quad (7.43)$$

and hence that *the Mandel stress* \mathbf{M}^e *is symmetric*.

Next, the spectral representation of \mathbf{C}^e is

$$\mathbf{C}^e = \sum_{i=1}^3 \omega_i^e \mathbf{r}_i^e \otimes \mathbf{r}_i^e, \quad \text{with} \quad \omega_i^e = \lambda_i^{e2}, \quad (7.44)$$

where $(\mathbf{r}_1^e, \mathbf{r}_2^e, \mathbf{r}_3^e)$ are the orthonormal eigenvectors of \mathbf{C}^e and \mathbf{U}^e , and $(\lambda_1^e, \lambda_2^e, \lambda_3^e)$ are the positive eigenvalues of \mathbf{U}^e . Instead of using the invariants $\mathcal{I}_{\mathbf{C}^e}$, the free energy $\check{\psi}_{\mathbf{R}}$ for isotropic materials may be alternatively expressed in terms of the principal stretches and temperature as

$$\psi_{\mathbf{R}} = \check{\psi}_{\mathbf{R}}(\lambda_1^e, \lambda_2^e, \lambda_3^e, \vartheta, c_{\mathbf{R}}, \xi). \quad (7.45)$$

Then, by the chain-rule and (7.4)₂, the stress \mathbf{T}^e is given by

$$\mathbf{T}^e = 2 \frac{\partial \check{\psi}_{\mathbf{R}}(\lambda_1^e, \lambda_2^e, \lambda_3^e, \vartheta, c_{\mathbf{R}}, \xi)}{\partial \mathbf{C}^e} = 2 \sum_{i=1}^3 \frac{\partial \check{\psi}_{\mathbf{R}}(\lambda_1^e, \lambda_2^e, \lambda_3^e, \vartheta, c_{\mathbf{R}}, \xi)}{\partial \lambda_i^e} \frac{\partial \lambda_i^e}{\partial \mathbf{C}^e} = \sum_{i=1}^3 \frac{1}{\lambda_i^e} \frac{\partial \check{\psi}_{\mathbf{R}}(\lambda_1^e, \lambda_2^e, \lambda_3^e, \vartheta, c_{\mathbf{R}}, \xi)}{\partial \lambda_i^e} \frac{\partial \omega_i}{\partial \mathbf{C}^e}. \quad (7.46)$$

Assume that the squared principal stretches ω_i^e are distinct, so that the ω_i^e and the principal directions \mathbf{r}_i^e may be considered as functions of \mathbf{C}^e ; then

$$\frac{\partial \omega_i^e}{\partial \mathbf{C}^e} = \mathbf{r}_i^e \otimes \mathbf{r}_i^e, \quad (7.47)$$

and, granted this, (7.47) and (7.46) imply that

$$\mathbf{T}^e = \sum_{i=1}^3 \frac{1}{\lambda_i^e} \frac{\partial \check{\psi}_{\mathbf{R}}(\lambda_1^e, \lambda_2^e, \lambda_3^e, \vartheta, c_{\mathbf{R}}, \xi)}{\partial \lambda_i^e} \mathbf{r}_i^e \otimes \mathbf{r}_i^e. \quad (7.48)$$

Further, from (6.10),

$$\mathbf{T} = J^{-1} \mathbf{F}^e \mathbf{T}^e \mathbf{F}^{e\top} = J^{-1} \mathbf{R}^e \mathbf{U}^e \mathbf{T}^e \mathbf{U}^e \mathbf{R}^{e\top} = J^{-1} \mathbf{R}^e \left(\sum_{i=1}^3 \lambda_i^e \frac{\partial \check{\psi}_{\mathbf{R}}(\lambda_1^e, \lambda_2^e, \lambda_3^e, \vartheta, c_{\mathbf{R}}, \xi)}{\partial \lambda_i^e} \mathbf{r}_i^e \otimes \mathbf{r}_i^e \right) \mathbf{R}^{e\top}. \quad (7.49)$$

Next, since $\mathbf{M}^e = \mathbf{C}^e \mathbf{T}^e$, use of (7.44) and (7.48) gives the Mandel stress as

$$\mathbf{M}^e = \sum_{i=1}^3 \lambda_i^e \frac{\partial \check{\psi}_{\mathbf{R}}(\lambda_1^e, \lambda_2^e, \lambda_3^e, \vartheta, c_{\mathbf{R}}, \xi)}{\partial \lambda_i^e} \mathbf{r}_i^e \otimes \mathbf{r}_i^e. \quad (7.50)$$

Let

$$\mathbf{E}^e \stackrel{\text{def}}{=} \ln \mathbf{U}^e = \sum_{i=1}^3 E_i^e \mathbf{r}_i^e \otimes \mathbf{r}_i^e, \quad (7.51)$$

denote the logarithmic elastic strain with principal values

$$E_i^e \stackrel{\text{def}}{=} \ln \lambda_i^e, \quad (7.52)$$

and consider an elastic free energy function of the form

$$\check{\psi}_{\mathbf{R}}(\lambda_1^e, \lambda_2^e, \lambda_3^e, \vartheta, c_{\mathbf{R}}, \xi) = \check{\psi}_{\mathbf{R}}(E_1^e, E_2^e, E_3^e, \vartheta, c_{\mathbf{R}}, \xi), \quad (7.53)$$

so that, using (7.50),

$$\mathbf{M}^e = \sum_{i=1}^3 \frac{\partial \check{\psi}_{\mathbf{R}}(E_1^e, E_2^e, E_3^e, \vartheta, c_{\mathbf{R}}, \xi)}{\partial E_i^e} \mathbf{r}_i^e \otimes \mathbf{r}_i^e. \quad (7.54)$$

With the logarithmic elastic strain defined by (7.51), and bearing (7.53) and (7.54), for isotropic elastic materials we henceforth consider a free energy of the form

$$\psi_{\mathbf{R}} = \hat{\psi}_{\mathbf{R}}(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_{\mathbf{R}}, \xi) \quad (7.55)$$

with $\mathcal{I}_{\mathbf{E}^e}$ a list of principal invariants of \mathbf{E}^e , or equivalently a list of principal values of \mathbf{E}^e . The Mandel stress is then given by

$$\mathbf{M}^e = \frac{\partial \hat{\psi}_{\mathbf{R}}(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_{\mathbf{R}}, \xi)}{\partial \mathbf{E}^e}, \quad (7.56)$$

and using (7.49) the corresponding Cauchy stress is given by

$$\mathbf{T} = J^{-1} \mathbf{R}^e \mathbf{M}^e \mathbf{R}^{e\top}. \quad (7.57)$$

7.5 Plastic flow rule for isotropic materials

Recall the constitutive equation (7.11)₁ for the plastic stretchings \mathbf{D}_α^p ,

$$\mathbf{D}_\alpha^p = \bar{\mathbf{D}}_\alpha^p(\mathbf{M}_0^e, \vartheta, S_\alpha) = \bar{d}_\alpha^p(\mathbf{M}_0^e, \vartheta, S_\alpha) \bar{\mathbf{N}}_\alpha^p(\mathbf{M}^e, \vartheta, S_\alpha). \quad (7.58)$$

We now make two major assumptions concerning the plastic flow for isotropic materials:

(1) **Codirectionality hypothesis:**

Guided by (7.13), we assume henceforth that each direction of plastic flow $\bar{\mathbf{N}}_\alpha^p$ is parallel to and points in the same direction as \mathbf{M}_0^e , so that

$$\bar{\mathbf{N}}_\alpha^p = \frac{\mathbf{M}_0^e}{|\mathbf{M}_0^e|}. \quad (7.59)$$

Further, note that on account of the isotropy of $\bar{\mathbf{D}}_\alpha^p$, the scalar flow rate function $\bar{d}_\alpha^p(\mathbf{M}^e, \vartheta, S_\alpha)$ is also isotropic, and has the representation

$$d_\alpha^p = \bar{d}_\alpha^p(\mathcal{I}_{\mathbf{M}_0^e}, \vartheta, S_\alpha) \geq 0, \quad (7.60)$$

where $\mathcal{I}_{\mathbf{M}_0^e}$ is the list of principal invariants of \mathbf{M}_0^e .

Note that in our *homogenized model*, on account of (7.59) the plastic flow directions for the bond-coat and the oxide are *identical*

$$\bar{\mathbf{N}}_{\text{bc}}^p = \bar{\mathbf{N}}_{\text{ox}}^p = \frac{\mathbf{M}_0^e}{|\mathbf{M}_0^e|} \equiv \mathbf{N}^p, \quad (7.61)$$

and henceforth denoted by \mathbf{N}^p . A further consequence of (7.59) and (7.61) is that from the definition (7.14) for the resolved Mandel stress, we have that the resolved stresses in the bond-coat and the oxide are also the same,

$$\bar{\tau}_{\text{bc}} = \bar{\tau}_{\text{ox}} = \mathbf{N}^p : \mathbf{M}_0^e = |\mathbf{M}_0^e| \equiv \bar{\tau}. \quad (7.62)$$

(2) **Strong isotropy hypothesis:**

We also assume that each scalar function $h_\alpha(d_\alpha^p, \mathbf{N}^p, \vartheta, S_\alpha)$ characterizing the evolution of the scalar internal variable S_α is independent of the flow direction \mathbf{N}^p , so that

$$h_\alpha(d_\alpha^p, \vartheta, S_\alpha). \quad (7.63)$$

Henceforth, for convenience, we replace $\bar{\tau} = |\mathbf{M}_0^e|$ by

$$\bar{\tau} \stackrel{\text{def}}{=} \frac{1}{\sqrt{2}} |\mathbf{M}_0^e|, \quad (7.64)$$

and call this newly defined quantity an *equivalent shear stress*. We define *equivalent plastic shear rates* for the bond-coat and oxide by

$$\nu_\alpha^p \stackrel{\text{def}}{=} \sqrt{2} d_\alpha^p. \quad (7.65)$$

Then, using (7.64), (7.65), and (7.59), the plastic stretchings \mathbf{D}_α^p in (7.58) may be written as

$$\mathbf{D}_\alpha^p = \nu_\alpha^p \left(\frac{\mathbf{M}_0^e}{2\bar{\tau}} \right), \quad (7.66)$$

with

$$\nu_\alpha^p = \bar{\nu}_\alpha^p(\mathcal{I}_{\mathbf{M}_0^e}, \vartheta, S_\alpha) \geq 0. \quad (7.67)$$

In accordance with prior experience, we henceforth neglect any dependence of viscoplastic flow on $\det \mathbf{M}_0^e$, and assume that the equivalent plastic shear strain rates are given by

$$\nu_\alpha^p = \bar{\nu}_\alpha^p(\bar{\tau}, \vartheta, S_\alpha) \geq 0. \quad (7.68)$$

Further, in view of (7.63) and (7.65), the evolution equations of the resistances S_α are taken to be given by

$$\dot{S}_\alpha = h_\alpha(\nu_\alpha^p, \vartheta, S_\alpha). \quad (7.69)$$

Finally, since the directions of plastic flow are identical, it is suitable to introduce an overall equivalent plastic shear strain rate

$$\nu^p = \omega \nu_{ox}^p + (1 - \omega) \nu_{bc}^p, \quad (7.70)$$

and an overall equivalent plastic shear strain

$$\gamma^p = \int_0^t \nu^p(\tau) d\tau. \quad (7.71)$$

7.6 Stress-modulated swelling due to the oxidation reaction

The spectral decomposition of \mathbf{M}^e is given by

$$\mathbf{M}^e = \sum_{i=1}^3 \sigma_i \hat{\mathbf{r}}_i \otimes \hat{\mathbf{r}}_i \quad (7.72)$$

where $\{\sigma_i | i = 1, 2, 3\}$ are the principal values. We assume that the principal stresses are strictly ordered such that

$$\sigma_1 \geq \sigma_2 \geq \sigma_3.$$

We allow for a possibility of unequal rates of swelling with respect to the principal directions of stress, and assume that

$$\mathbb{S} = \sum_{i=1}^3 \beta_i \hat{\mathbf{r}}_i \otimes \hat{\mathbf{r}}_i, \quad \text{with} \quad \beta_i = \hat{\beta}_i(\sigma_i). \quad (7.73)$$

For future use, we write

$$\beta \stackrel{\text{def}}{=} \frac{1}{3} \text{tr} \mathbb{S} = \frac{1}{3} (\beta_1 + \beta_2 + \beta_3), \quad (7.74)$$

as a *mean volumetric strain due to swelling*. This mean volumetric strain may be related to the classical *Pilling-Bedworth ratio* in the Materials Science literature, as follows.

Consider an element M whose oxide has composition $M_a O_b$. The *Pilling-Bedworth ratio* (Pilling and Bedworth, 1923) for the oxide is defined as

$$J_{\text{PB}} \stackrel{\text{def}}{=} \frac{V_{M_a O_b}}{a V_M} = \frac{\mathcal{M}_{M_a O_b} \rho_M}{a \mathcal{M}_M \rho_{M_a O_b}}, \quad (7.75)$$

where $V_{M_a O_b}$ is the molar volume of the oxide, and V_M is the molar volume of the element M . Also, $\mathcal{M}_{M_a O_b}$ is the molar mass of $M_a O_b$, \mathcal{M}_M is the molar mass of M , and $\rho_{M_a O_b}$ and ρ_M are the mass densities of the oxide $M_a O_b$ and the element M , respectively. For Al_2O_3 ,

$$J_{\text{PB}} = \frac{V_{\text{Al}_2\text{O}_3}}{2V_{\text{Al}}} = 1.28, \quad (7.76)$$

a value which is well in excess of unity. The mean volumetric strain, β , is related to Pilling-Bedworth ratio, J_{PB} , by

$$\beta = \frac{1}{3} \ln(J_{\text{PB}}). \quad (7.77)$$

8 Summary

In this section we summarize our isotropic chemo-thermo-mechanically coupled theory. The theory relates the following basic fields:

$\mathbf{x} = \chi(\mathbf{X}, t),$	motion;
$\mathbf{F} = \nabla\chi, \quad J = \det \mathbf{F} > 0,$	deformation gradient;
$\mathbf{F} = \mathbf{F}^e \mathbf{F}^i,$	multiplicative decomposition of \mathbf{F} ;
$\mathbf{F}^e, \quad J^e = \det \mathbf{F}^e > 0,$	elastic distortion;
$\mathbf{F}^i, \quad J^i = \det \mathbf{F}^i > 0,$	inelastic distortion;
$\mathbf{F}^e = \mathbf{R}^e \mathbf{U}^e,$	polar decomposition of \mathbf{F}^e ;
$\mathbf{C}^e = \mathbf{F}^{e\top} \mathbf{F}^e = \mathbf{U}^{e2},$	elastic right Cauchy-Green tensor;
$\mathbf{U}^e = \sum_{\alpha=1}^3 \lambda_{\alpha}^e \mathbf{r}_{\alpha}^e \otimes \mathbf{r}_{\alpha}^e,$	spectral decomposition of \mathbf{U}^e ;
$\mathbf{E}^e = \sum_{\alpha=1}^3 (\ln \lambda_{\alpha}^e) \mathbf{r}_{\alpha}^e \otimes \mathbf{r}_{\alpha}^e,$	logarithmic elastic strain;
$\mathbf{T} = \mathbf{T}^{\top},$	Cauchy stress;
$\mathbf{T}^e = J \mathbf{F}^{e-1} \mathbf{T} \mathbf{F}^{e-\top},$	elastic second Piola stress;
$\mathbf{M}^e = \mathbf{C}^e \mathbf{T}^e,$	Mandel stress;
$\mathbf{T}_{\mathbf{R}} = J \mathbf{T} \mathbf{F}^{-\top},$	Piola stress;
$\psi_{\mathbf{R}},$	free energy density per unit reference volume;
$\eta_{\mathbf{R}},$	entropy density per unit reference volume;
$\vartheta > 0,$	absolute temperature;
$\nabla\vartheta,$	referential temperature gradient;
$\mathbf{q}_{\mathbf{R}},$	referential heat flux vector;
$c_{\mathbf{R}},$	molecular concentration per unit reference volume;
$\mu,$	chemical potential;
$\nabla\mu,$	referential gradient of chemical potential;
$\mathbf{j}_{\mathbf{R}},$	referential species flux vector;
$\xi \in [0, 1],$	local volume fraction of oxide;
$S_{\text{bc}}, S_{\text{ox}},$	scalar hardening variables.

8.1 Constitutive equations

1. Free energy

$$\psi_{\mathbf{R}} = \hat{\psi}_{\mathbf{R}}(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_{\mathbf{R}}, \xi), \quad (8.1)$$

where $\mathcal{I}_{\mathbf{E}^e}$ represents a list of the principal invariants of the elastic strain \mathbf{E}^e .

2. Cauchy stress. Mandel stress

The Cauchy stress is given by

$$\mathbf{T} \stackrel{\text{def}}{=} J^{-1} (\mathbf{R}^e \mathbf{M}^e \mathbf{R}^{e\top}), \quad (8.2)$$

where

$$\mathbf{M}^e = \frac{\partial \hat{\psi}_{\mathbf{R}}(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_{\mathbf{R}}, \xi)}{\partial \mathbf{E}^e}, \quad (8.3)$$

is the Mandel stress, which, on account of the isotropy of $\bar{\psi}_{\mathbf{R}}$ is *symmetric*. The spectral decomposition of \mathbf{M}^e is given by

$$\mathbf{M}^e = \sum_{i=1}^3 \sigma_i \hat{\mathbf{r}}_i \otimes \hat{\mathbf{r}}_i, \quad (8.4)$$

where $\{\sigma_i | i = 1, 2, 3\}$ are the principal values and $\{\hat{\mathbf{r}}_i | i = 1, 2, 3\}$ are the corresponding orthonormal principal directions. We assume that the principal stresses are strictly ordered such that

$$\sigma_1 \geq \sigma_2 \geq \sigma_3.$$

Further, the *equivalent shear stress* is defined by

$$\bar{\tau} \stackrel{\text{def}}{=} \frac{1}{\sqrt{2}} |\mathbf{M}_0^e|, \quad (8.5)$$

and the elastic second Piola stress is given by

$$\mathbf{T}^e = \mathbf{C}^{e-1} \mathbf{M}^e. \quad (8.6)$$

3. Entropy. Chemical potential. Affinity

The partial derivatives of the free energy

$$\left. \begin{aligned} \eta_{\mathbf{R}} &= -\frac{\partial \hat{\psi}_{\mathbf{R}}(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_{\mathbf{R}}, \xi)}{\partial \vartheta}, \\ \mu &= \frac{\partial \hat{\psi}_{\mathbf{R}}(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_{\mathbf{R}}, \xi)}{\partial c_{\mathbf{R}}}, \\ \mathcal{A} &= -\frac{\partial \hat{\psi}_{\mathbf{R}}(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_{\mathbf{R}}, \xi)}{\partial \xi}, \end{aligned} \right\} \quad (8.7)$$

respectively, represent the entropy, chemical potential, and a thermodynamic force related to the oxide volume fraction ξ , which we call the *affinity* of the oxidation reaction.

4. Flow rule

With $\xi(\mathbf{X}, t) \in [0, 1]$ the local *volume fraction of the oxide* at \mathbf{X} , the evolution equation for \mathbf{F}^i is

$$\dot{\mathbf{F}}^i = \left(\mathbf{D}^s + (1 - \omega) \mathbf{D}_{\text{bc}}^p + \omega \mathbf{D}_{\text{ox}}^p \right) \mathbf{F}^i, \quad (8.8)$$

where

(i) \mathbf{D}^s is given by

$$\mathbf{D}^s = \dot{\xi} \mathbb{S}, \quad \dot{\xi} \geq 0, \quad (8.9)$$

where

$$\mathbb{S} = \sum_{i=1}^3 \beta_i \hat{\mathbf{r}}_i \otimes \hat{\mathbf{r}}_i, \quad \text{with} \quad \beta_i = \hat{\beta}_i(\sigma_i), \quad (8.10)$$

gives the direction and magnitude of the swelling strain accompanying the chemical reaction. Further, with

$$\mathcal{F} \stackrel{\text{def}}{=} \mathcal{A} + \mathbf{M}^e : \mathbb{S}, \quad (8.11)$$

where the transformation rate $\dot{\xi}$ is given by a constitutive equation

$$\dot{\xi} = \bar{\xi}(\mathcal{F}, \vartheta, \xi) \geq 0, \quad (8.12)$$

with $\mathcal{F} \dot{\xi} > 0$ whenever $\dot{\xi} > 0$.

(ii) \mathbf{D}_{bc}^p is given by

$$\mathbf{D}_{\text{bc}}^p = \nu_{\text{bc}}^p \left(\frac{\mathbf{M}_0^e}{2\bar{\tau}} \right) \quad (8.13)$$

with ν_{bc}^p given by a constitutive equation

$$\nu_{\text{bc}}^p = \bar{\nu}_{\text{bc}}^p(\bar{\tau}, \vartheta, S_{\text{bc}}) \geq 0, \quad (8.14)$$

with $\bar{\tau} \nu_{\text{bc}}^p > 0$ whenever $\nu_{\text{bc}}^p > 0$.

(iii) \mathbf{D}_{ox}^p is given by

$$\mathbf{D}_{\text{ox}}^p = \nu_{\text{ox}}^p \left(\frac{\mathbf{M}_0^e}{2\bar{\tau}} \right) \quad (8.15)$$

with ν_{ox}^p given by a constitutive equation

$$\nu_{\text{ox}}^p = \bar{\nu}_{\text{ox}}^p(\bar{\tau}, \vartheta, S_{\text{ox}}) \geq 0, \quad (8.16)$$

with $\bar{\tau}\nu_{\text{ox}}^p > 0$ whenever $\nu_{\text{ox}}^p > 0$.

(iv) $\omega(\xi)$ represents a response function that characterizes the nature of plastic flow during the oxidation reaction and is given by

$$\omega = \bar{\omega}(\xi) \quad (8.17)$$

with $\bar{\omega}(0) = 0$ and $\bar{\omega}(1) = 1$.

5. Evolution equations for internal variables S_{bc} and S_{ox}

$$\dot{S}_{\text{bc}} = h_{\text{bc}}(\nu_{\text{bc}}^p, \vartheta, S_{\text{bc}}), \quad \text{and} \quad \dot{S}_{\text{ox}} = h_{\text{bc}}(\nu_{\text{ox}}^p, \vartheta, S_{\text{ox}}). \quad (8.18)$$

The evolution equations for \mathbf{F}^i , ξ , S_{bc} , and S_{ox} need to be accompanied by initial conditions. Typical initial conditions presume that the body is initially (at time $t = 0$, say) in a **virgin state** in the sense that

$$\mathbf{F}(\mathbf{X}, 0) = \mathbf{F}^i(\mathbf{X}, 0) = \mathbf{1}, \quad \xi(\mathbf{X}, 0) = 0, \quad S_{\text{bc}}(\mathbf{X}, 0) = S_{\text{bc},0} (= \text{const.}), \quad S_{\text{ox}}(\mathbf{X}, 0) = S_{\text{ox},0} (= \text{const.}) \quad (8.19)$$

so that by $\mathbf{F} = \mathbf{F}^e \mathbf{F}^i$ we also have $\mathbf{F}^e(\mathbf{X}, 0) = \mathbf{1}$.

6. Fourier's Law

The heat flux \mathbf{q}_{R} is presumed to obey Fourier's law,

$$\mathbf{q}_{\text{R}} = -\kappa \nabla \vartheta, \quad (8.20)$$

with $\kappa(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_{\text{R}}, \xi) > 0$ the thermal conductivity.

7. Fick's Law

The species flux \mathbf{j}_{R} is presumed to obey Fick's law

$$\mathbf{j}_{\text{R}} = -m \nabla \mu, \quad (8.21)$$

with $m(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_{\text{R}}, \xi) > 0$ the species mobility.

8.2 Governing partial differential equations

The governing partial differential equations consist of:

1. The local force balance (4.2), viz.

$$\text{Div } \mathbf{T}_{\text{R}} + \mathbf{b}_{\text{R}} = \mathbf{0}, \quad (8.22)$$

where $\mathbf{T}_{\text{R}} = J\mathbf{T}\mathbf{F}^{-\top}$ is the Piola stress, with \mathbf{T} given by (8.3) and (8.2), and \mathbf{b}_{R} is the non-inertial body force.

2. The local balance of energy (7.27), which, together with (8.20) and (8.21), gives the following partial differential equation for the temperature

$$c\dot{\vartheta} = \text{Div}(\kappa \nabla \vartheta) + q_{\text{R}} + (1 - \omega) \bar{\tau} \nu_{\text{bc}}^p + \omega \bar{\tau} \nu_{\text{ox}}^p + \mathcal{F} \dot{\xi} + m |\nabla \mu|^2 + \frac{1}{2} \vartheta \frac{\partial \mathbf{T}^e}{\partial \vartheta} : \dot{\mathbf{C}}^e + \vartheta \frac{\partial \mu}{\partial \vartheta} \dot{c}_{\text{R}} - \vartheta \frac{\partial \mathcal{A}}{\partial \vartheta} \dot{\xi}, \quad (8.23)$$

in which

$$c = -\vartheta \frac{\partial^2 \hat{\psi}(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_{\text{R}}, \xi)}{\partial \vartheta^2} \quad (8.24)$$

is the specific heat.

3. The local balance equation for the concentration of diffusing species (5.4), which, together with (8.21), gives

$$\dot{c}_R = \text{Div} (m \nabla \mu). \quad (8.25)$$

9 Specialization of the constitutive equations

The theory presented thus far is quite general. Since the precise nature of the various coupling effects have not been completely elucidated in the existing literature, we now introduce special constitutive equations which should provide a suitable beginning for analysis and future refinement.

9.1 Free energy

We consider a separable free energy of the form

$$\hat{\psi}_R(\mathbf{E}^e, \vartheta, c_R, \xi) = \psi^e(\mathbf{E}^e, \vartheta, \xi) + \psi^{\text{chem}}(\vartheta, \xi) + \psi^{\text{diff}}(\vartheta, c_R). \quad (9.1)$$

Here:

- (i) ψ^e is a thermo-elastic energy given by

$$\psi^e(\mathbf{E}^e, \vartheta, \xi) = G|\mathbf{E}^e|^2 + \frac{1}{2}(K - \frac{2}{3}G)(\text{tr} \mathbf{E}^e)^2 - (\vartheta - \vartheta_0)(3K\alpha)(\text{tr} \mathbf{E}^e) + c(\vartheta - \vartheta_0) - c\vartheta \ln\left(\frac{\vartheta}{\vartheta_0}\right), \quad (9.2)$$

which is a simple generalization of the classical strain energy function of infinitesimal isotropic elasticity⁵ combined with an entropic contribution. The parameters

$$\begin{aligned} G(\vartheta, \xi) &= (1 - \xi)G_{\text{bc}}(\vartheta) + \xi G_{\text{ox}}(\vartheta) > 0, \\ K(\vartheta, \xi) &= (1 - \xi)K_{\text{bc}}(\vartheta) + \xi K_{\text{ox}}(\vartheta) > 0, \\ \alpha(\vartheta, \xi) &= (1 - \xi)\alpha_{\text{bc}}(\vartheta) + \xi \alpha_{\text{ox}}(\vartheta) > 0, \end{aligned} \quad (9.3)$$

are the shear modulus, bulk modulus, and coefficient of thermal expansion, respectively, and $c > 0$ is a constant specific heat. Also, ϑ_0 is a *reference temperature*, which is to be taken as a nominal elevated temperature of interest in the range $\approx 900\text{--}1100^\circ\text{C}$.

- (ii) ψ^{chem} is a chemical energy related to the oxidation reaction, taken to be given by

$$\psi^{\text{chem}} = \frac{1}{2}H(1 - \xi)^2, \quad (9.4)$$

where the parameter $H(\vartheta) > 0$ is a *chemistry modulus*. This term in the free energy favors the local state $\xi = 1$.⁶

- (iii) ψ^{diff} is another chemical energy related to species diffusion, taken to be given by

$$\psi^{\text{diff}} = \mu^0 c_R + R\vartheta c_R (\ln \tilde{c}_R - 1), \quad (9.5)$$

where μ^0 is a reference chemical potential, \tilde{c}_R is a normalized oxygen concentration given by

$$\tilde{c}_R \stackrel{\text{def}}{=} \frac{c_R}{N_{\text{bc}}} \quad (9.6)$$

with

$$N_{\text{bc}} \stackrel{\text{def}}{=} \frac{\rho_{\text{bc}}}{\mathcal{M}_{\text{bc}}} \quad (9.7)$$

the initial number of moles of bond coat material per unit reference volume and \mathcal{M}_{bc} the molar mass of the bond coat, and R is the universal gas constant.

⁵This is a useful free energy formulation for *moderately large elastic stretches* (Anand, 1979; Anand, 1986).

⁶This special form for ψ^{chem} is motivated by the paper of Ulm et al. (2000) on chemo-mechanics of alkali-silica reactions and their effects on deterioration of concrete structures.

Thus

$$\begin{aligned} \psi_{\text{R}} = G|\mathbf{E}^e|^2 + \frac{1}{2}(K - \frac{2}{3}G)(\text{tr}\mathbf{E}^e)^2 - (\vartheta - \vartheta_0)(3K\alpha)(\text{tr}\mathbf{E}^e) + c(\vartheta - \vartheta_0) - c\vartheta \ln\left(\frac{\vartheta}{\vartheta_0}\right) \\ + \frac{1}{2}H(1 - \xi)^2 + \mu^0 c_{\text{R}} + R\vartheta c_{\text{R}}(\ln \tilde{c}_{\text{R}} - 1). \end{aligned} \quad (9.8)$$

Then, by (8.3) and (8.7), the Mandel stress, the entropy, the chemical potential, and the affinity are given by

$$\begin{aligned} \mathbf{M}^e &= 2G\mathbf{E}_0^e + K(\text{tr}\mathbf{E}^e)\mathbf{1} - 3K\alpha(\vartheta - \vartheta_0)\mathbf{1}, \\ \eta_{\text{R}} &= c \ln\left(\frac{\vartheta}{\vartheta_0}\right) + 3K\alpha(\text{tr}\mathbf{E}^e) - \frac{1}{2}\frac{\partial H}{\partial \vartheta}(1 - \xi)^2 - R c_{\text{R}}(\ln \tilde{c}_{\text{R}} - 1) - A, \\ \mu &= \mu^0 + R\vartheta \ln \tilde{c}_{\text{R}}, \\ A &= H(1 - \xi) - B, \end{aligned} \quad (9.9)$$

where

$$A = \frac{\partial G}{\partial \vartheta}|\mathbf{E}^e|^2 + \frac{1}{2}\left(\frac{\partial K}{\partial \vartheta} - \frac{2}{3}\frac{\partial G}{\partial \vartheta}\right)(\text{tr}\mathbf{E}^e)^2 - 3(\vartheta - \vartheta_0)\left(\frac{\partial K}{\partial \vartheta}\alpha + K\frac{\partial \alpha}{\partial \vartheta}\right)(\text{tr}\mathbf{E}^e) \quad (9.10)$$

and

$$\begin{aligned} B = (G_{\text{ox}} - G_{\text{bc}})|\mathbf{E}^e|^2 + \frac{1}{2}\left((K_{\text{ox}} - K_{\text{bc}}) - \frac{2}{3}(G_{\text{ox}} - G_{\text{bc}})\right)(\text{tr}\mathbf{E}^e)^2 \\ - 3(\vartheta - \vartheta_0)((K_{\text{ox}} - K_{\text{bc}})\alpha + K(\alpha_{\text{ox}} - \alpha_{\text{bc}}))\text{tr}\mathbf{E}^e \end{aligned} \quad (9.11)$$

account for the variation of the thermoelastic moduli with temperature ϑ and the volume fraction of oxide ξ , respectively.

9.2 Viscoplastic deformation of the bond-coat and the oxide

For the flow functions (8.14) and (8.16) which specify the equivalent plastic shear strain rates, we choose thermally activated relations with power-law stress dependence,

$$\nu_{\text{bc}}^p = \begin{cases} 0 & \text{if } \bar{\tau} = 0, \\ \nu_{\text{bc}}^0 \exp\left(\frac{-Q_{\text{bc}}}{R\vartheta}\right) \left(\frac{\bar{\tau}}{S_{\text{bc}}}\right)^{n_{\text{bc}}} & \text{if } \bar{\tau} > 0, \end{cases} \quad (9.12)$$

for the bond-coat, and

$$\nu_{\text{ox}}^p = \begin{cases} 0 & \text{if } \bar{\tau} = 0, \\ \nu_{\text{ox}}^0 \exp\left(\frac{-Q_{\text{ox}}}{R\vartheta}\right) \left(\frac{\bar{\tau}}{S_{\text{ox}}}\right)^{n_{\text{ox}}} & \text{if } \bar{\tau} > 0, \end{cases} \quad (9.13)$$

for the oxide. In (9.12) and (9.13), ν_{α}^0 are reference shear strain rates, Q_{α} are activation energies, n_{α} are creep-exponents, respectively, and R is the universal gas constant. The stress-dimensioned variables S_{bc} and S_{ox} represent *creep strengths*.

If we *neglect primary creep*, and accordingly assume that the internal variables S_{bc} and S_{ox} are *constants*, then equations (9.12) and (9.13) represent *steady-state creep rates*. Under these conditions the relations (9.12) and (9.13) may be written as

$$\nu_{\text{bc}}^p = \begin{cases} 0 & \text{if } \bar{\tau} = 0, \\ C_{\text{bc}} \exp\left(\frac{-Q_{\text{bc}}}{R\vartheta}\right) (\bar{\tau})^{n_{\text{bc}}}, & \text{with } C_{\text{bc}} \stackrel{\text{def}}{=} \frac{\nu_{\text{bc}}^p}{S_{\text{bc}}^{n_{\text{bc}}}}, \quad \text{if } \bar{\tau} > 0, \end{cases} \quad (9.14)$$

for the bond-coat, and

$$\nu^p_{\text{ox}} = \begin{cases} 0 & \text{if } \bar{\tau} = 0, \\ C_{\text{ox}} \exp\left(\frac{-Q_{\text{bc}}}{R\vartheta}\right) (\bar{\tau})^{n_{\text{ox}}}, & \text{with } C_{\text{ox}} \stackrel{\text{def}}{=} \frac{\nu^p_{\text{ox}}}{S_{\text{bc}}^{n_{\text{ox}}}}, \quad \text{if } \bar{\tau} > 0; \end{cases} \quad (9.15)$$

for the oxide. The constants C_α have units of $1/(\text{s MPa}^{n_\alpha})$, and the activation energies Q_α have units of kJ/mol.

Finally, we need to specify the response function $\omega(\xi)$ (cf. (2.15)) in the transition zone where the oxidation reaction is in progress. The simplest assumption would be to set $\omega = \xi$. However, in this case since the metallic bond-coat material has a much higher propensity to creep than the oxide, the contribution from the viscoplastic shearing rate of the bond coat, ν^p_{bc} , will dominate the overall viscoplastic shearing rate, ν^p (cf. (7.70)). As a result, the inelastic swelling deformation due to oxidation can easily be ‘‘compensated’’ for by the corresponding viscoplastic deformation of the bond-coat/oxide mixture, and this would not lead to the development of significant stresses due to the oxidation reaction — which is in disagreement with the well-documented development of significant growth stresses which are produced due to the volumetric expansion from oxidation (cf., e.g., Tolpygo and Clarke, 1998.) To the knowledge of the authors, the nature of viscoplastic deformation at a material point that is in the process of oxidizing is not well-known. However, it is clear that when the material point has fully oxidized it will have the creep properties of the oxide. For this reason, and for simplicity, we assume that as soon as a material point starts to oxidize, its creep rate is determined by that of the oxide. Accordingly, we assume that

$$\omega = \begin{cases} 0 & \text{if } \xi = 0, \\ 1 & \text{otherwise.} \end{cases} \quad (9.16)$$

9.3 Oxide growth. Evolution of ξ

A fundamental open physical question in bondcoat oxidation is the directionality of the oxidation, that is in a specification of the tensor \mathbb{S} . A specification of the growth-direction tensor \mathbb{S} and its dependence on the local stress and microstructural state has been a topic of research in the past decade (cf., e.g., Huntz et al., 2002; Clarke, 2003), and there is some indication in the literature that the oxide growth occurs in a fashion such that that $\beta_1 \neq \beta_2 \neq \beta_3$, and that the local microstructure also has a significant influence on \mathbb{S} . However, such evidence is sparse, and not conclusive. Here, for simplicity, we ignore any anisotropy due to microstructural effects, and also assume that⁷

$$\beta_1 = \beta_2 = \beta_3 \equiv \beta > 0 \quad (\text{constant}).$$

Therefore

$$\mathbb{S} = \beta \mathbf{1}, \quad (9.17)$$

and hence

$$\mathbf{D}^s = \dot{\xi} \beta \mathbf{1}, \quad \dot{\xi} \geq 0. \quad (9.18)$$

From (7.77) and (9.17) we note that

$$\beta = \frac{1}{3} \ln(J_{\text{PB}}), \quad (9.19)$$

where J_{PB} is the Pilling-Bedworth ratio for the oxidation reaction.

Next we specialize the evolution equation (8.12) for ξ . First, from (8.11), (9.9)_{3,4}, and (9.17), the dissipative force \mathcal{F} is given by

$$\mathcal{F} = H(1 - \xi) - B + \beta \text{tr} \mathbf{M}^e. \quad (9.20)$$

Further, let \mathcal{R} denote the amount c_{R} (per unit reference volume) of the diffusing species consumed by the complete chemical reaction. Thus, when $\xi = 1$ we have $c_{\text{R}} = \mathcal{R}$, and $\dot{\xi}$ is non-zero only as long as

$$\xi \leq \frac{c_{\text{R}}}{\mathcal{R}}, \quad (9.21)$$

⁷This assumption may be modified as more tangible physical evidence becomes available.

and

$$\mathcal{F} > 0. \quad (9.22)$$

Accordingly, we assume a simple thermally-activated relation for $\dot{\xi}$ with power-law dependence on \mathcal{F} :

$$\dot{\xi} = \begin{cases} C_\xi \exp\left(\frac{-Q_s}{R\vartheta}\right) (\mathcal{F})^{n_\xi} & \text{if } \xi < \frac{c_R}{\mathcal{R}} \text{ and } \mathcal{F} > 0, \\ 0 & \text{otherwise.} \end{cases} \quad (9.23)$$

Here the constant C_ξ has units of $1/(\text{s MPa}^{n_\xi})$, Q_s is an *activation energy for swelling* with units of kJ/mol, and $n_\xi > 0$ is a power-law constant for the reaction rate.

9.4 Heat flux. Species flux

From (8.20), we have that the heat flux is given by

$$\mathbf{q}_R = -\kappa \nabla \vartheta, \quad (9.24)$$

with $\kappa(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_R, \xi) > 0$ the thermal conductivity. At this point in time the dependence of the thermal conductivity on the elastic deformation and species concentration is not well understood, and we ignore any such dependence here and assume that

$$\kappa = (1 - \xi)\kappa_{bc} + \xi\kappa_{ox}, \quad (9.25)$$

where $\kappa_{bc}(\vartheta) > 0$ and $\kappa_{ox}(\vartheta) > 0$ are the temperature dependent thermal conductivities of the bond-coat and the oxide, respectively, which presumably are experimentally measurable.

Further, from (8.21) we have that the species flux is given by

$$\mathbf{j}_R = -m \nabla \mu, \quad (9.26)$$

with $m(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_R, \xi) > 0$ the species mobility. Thus, with the chemical potential μ given by (9.9), we may write (9.26) as

$$\mathbf{j}_R = -D(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_R, \xi) \nabla c_R, \quad \text{with} \quad D(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_R, \xi) \stackrel{\text{def}}{=} m(\mathcal{I}_{\mathbf{E}^e}, \vartheta, c_R, \xi) \times \frac{R\vartheta}{c_R}, \quad (9.27)$$

where D represents the *diffusivity*. As for the thermal conductivity, the dependence of the species diffusivity on the elastic deformation is not well understood; accordingly, we ignore any such dependence. Next, the diffusivity of the oxygen in the bond-coat is much smaller than that in the oxide,

$$D_{bc} \ll D_{ox}, \quad (9.28)$$

where, D_{bc} and D_{ox} are the species diffusivity in the bond-coat and the oxide, respectively, which presumably are experimentally measurable. In the transition zone, where the reaction is in progress and $0 < \xi < 1$, species diffusion is similarly small. Accordingly, we assume that

$$D(c_R, \vartheta, \xi) = \begin{cases} D_{ox}(c_R, \vartheta) & \text{if } \xi = 1, \\ D_{bc}(c_R, \vartheta) & \text{if } \xi < 1. \end{cases} \quad (9.29)$$

These diffusivities typically exhibit an exponential dependence on temperature

$$D_\alpha(c_R, \vartheta) = D_{0,\alpha}(c_R) \exp\left(-\frac{Q_{d,\alpha}}{R\vartheta}\right), \quad (9.30)$$

where $Q_{d,\alpha}$ represent the *activation energies* for diffusion of the species in the bond-coat and the oxide.

10 Governing partial differential equations for the specialized constitutive equations. Boundary conditions

The governing partial differential equations consist of:

1. The local force balance (8.22), viz.

$$\text{Div } \mathbf{T}_R + \mathbf{b}_R = \mathbf{0}, \quad (10.1)$$

where $\mathbf{T}_R = J\mathbf{T}\mathbf{F}^{-T}$ is the Piola stress, with \mathbf{T} given by (8.2) and (9.9)₁, and \mathbf{b}_R is the non-inertial body force.

2. The local balance of energy (8.23), which, together with (9.9)₃ and (9.27), gives the following partial differential equation for the temperature

$$c\dot{\vartheta} = \text{Div}(\kappa\nabla\vartheta) + q_R + (1 - \omega)\bar{\tau}\nu^p_{bc} + \omega\bar{\tau}\nu^p_{ox} + \mathcal{F}\dot{\xi} + D\frac{c_R}{R\vartheta}|\nabla\mu|^2 + \vartheta\frac{1}{2}\frac{\partial\mathbf{T}^e}{\partial\vartheta}:\dot{\mathbf{C}}^e - \vartheta\frac{\partial\mathcal{A}}{\partial\vartheta}\dot{\xi} \quad (10.2)$$

with ω given by (9.16).

3. The local balance equation for the concentration of diffusing species (8.25), which, using (9.27), may alternatively be written as

$$\dot{c}_R = \text{Div}(D\nabla c_R), \quad (10.3)$$

with the diffusivity D given by (9.29) and (9.30).

We also need initial and boundary conditions to complete the model. Let \mathcal{S}_1 and \mathcal{S}_2 be *complementary subsurfaces* of the boundary ∂B of the body B in the sense $\partial B = \mathcal{S}_1 \cup \mathcal{S}_2$ and $\mathcal{S}_1 \cap \mathcal{S}_2 = \emptyset$. Similarly let \mathcal{S}_{c_R} and \mathcal{S}_{j_R} be *complementary subsurfaces* of the boundary: $\partial B = \mathcal{S}_{c_R} \cup \mathcal{S}_{j_R}$ and $\mathcal{S}_{c_R} \cap \mathcal{S}_{j_R} = \emptyset$, and finally, let \mathcal{S}_ϑ and \mathcal{S}_{q_R} be *complementary subsurfaces* of the boundary: $\partial B = \mathcal{S}_\vartheta \cup \mathcal{S}_{q_R}$ and $\mathcal{S}_\vartheta \cap \mathcal{S}_{q_R} = \emptyset$. Then for a time interval $t \in [0, T]$ we consider a pair of boundary conditions in which the motion is specified on \mathcal{S}_1 and the surface traction on \mathcal{S}_2 :

$$\left. \begin{aligned} \chi &= \check{\chi} && \text{on } \mathcal{S}_1 \times [0, T], \\ \mathbf{T}_R \mathbf{n}_R &= \check{\mathbf{t}}_R && \text{on } \mathcal{S}_2 \times [0, T], \end{aligned} \right\} \quad (10.4)$$

another pair of boundary conditions in which the concentration is specified on \mathcal{S}_{c_R} and the species flux on \mathcal{S}_{j_R}

$$\left. \begin{aligned} c_R &= \check{c}_R && \text{on } \mathcal{S}_{c_R} \times [0, T], \\ -D(\nabla c_R) \cdot \mathbf{n}_R &= \check{j}_R && \text{on } \mathcal{S}_{j_R} \times [0, T], \end{aligned} \right\} \quad (10.5)$$

and a final pair of boundary conditions in which the temperature is specified on \mathcal{S}_ϑ and the heat flux on \mathcal{S}_{q_R}

$$\left. \begin{aligned} \vartheta &= \check{\vartheta} && \text{on } \mathcal{S}_\vartheta \times [0, T], \\ -\kappa(\nabla\vartheta) \cdot \mathbf{n}_R &= \check{q}_R && \text{on } \mathcal{S}_{q_R} \times [0, T], \end{aligned} \right\} \quad (10.6)$$

with $\check{\chi}$, $\check{\mathbf{t}}_R$, $\check{\vartheta}$, \check{q}_R , \check{c}_R , and \check{j}_R *prescribed* functions of \mathbf{X} and t , and the initial data

$$\chi(\mathbf{X}, 0) = \chi_0(\mathbf{X}), \quad c_R(\mathbf{X}, 0) = c_{R,0}(\mathbf{X}) \quad \text{and} \quad \vartheta(\mathbf{X}, 0) = \vartheta_0(\mathbf{X}) \quad \text{in} \quad B. \quad (10.7)$$

The coupled set of equations (10.1), (10.2), and (10.3), together with (10.4), (10.5), (10.6), and (10.7), yield an initial boundary-value problem for the motion $\chi(\mathbf{X}, t)$, the temperature $\vartheta(\mathbf{X}, t)$, and the chemical species concentration $c_R(\mathbf{X}, t)$.

11 Concluding Remarks

In this work, we have formulated a chemo-thermo-mechanically coupled theory that accounts for elastic-viscoplastic deformation, diffusion of a chemically reacting species, and volumetric swelling due to the chemical reaction. We are in the process of (i) conducting a literature search, as well as performing our own experiments (as needed) to determine the material parameters appearing in our theory, and (ii) numerically implementing our theory in a finite-element program. Once the theory is numerically implemented and validated, then the numerical simulation capability should provide an important ingredient for analyzing the evolution of the local stress and strain states which are important ingredients for the life-prediction and performance-improvement of TBCs.

Acknowledgements

The authors would like to thank the King Fahd University of Petroleum and Minerals in Dhahran, Saudi Arabia, for funding the research reported in this paper through the Center for Clean Water and Clean Energy at MIT and KFUPM. Technical discussions with Zuhair Gasem, Esteban Busso, and Franz Ulm are gratefully acknowledged.

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