A Simulation Engine for Mesoscopic Modeling of High Temperature Corrosion Processes

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Abstract

High temperature corrosion (HTC) [1] is a damage process taking place in metals exposed to corrosive gases at temperatures above 550 $^{\circ}$C. Mathematically, HTC is described by a reaction diffusion system (RDS). However, the reaction term in this model is not precisely known and must be approximated by using thermodynamic equilibrium data. This data in turn is computed by thermodynamics computation tools and takes most of the time of numerical simulation algorithms. To reduce the computational effort a flexible simulation engine for the simulation of HTC on a mesoscopic scale is presented. It is based on coupling a PDE solution algorithm with a thermodynamics manager for speeding up the computation by data interpolation and parallelization. Two examples will illustrate the performance of HTC simulation.

1   Introduction

Well known examples of high temperature components are turbine blades or chemical reactor parts. Usually, nickel based alloys with aluminum, titanium, chromium and other alloy components are used as constructive materials. The corrosive atmospheres can contain oxygen, nitrogen, carbon or sulphur. An important property of HTC is that no electrolyte needs to be present. Instead, the corroding atoms directly stick to the metal surface where they have two possibilities (Figure 1) :
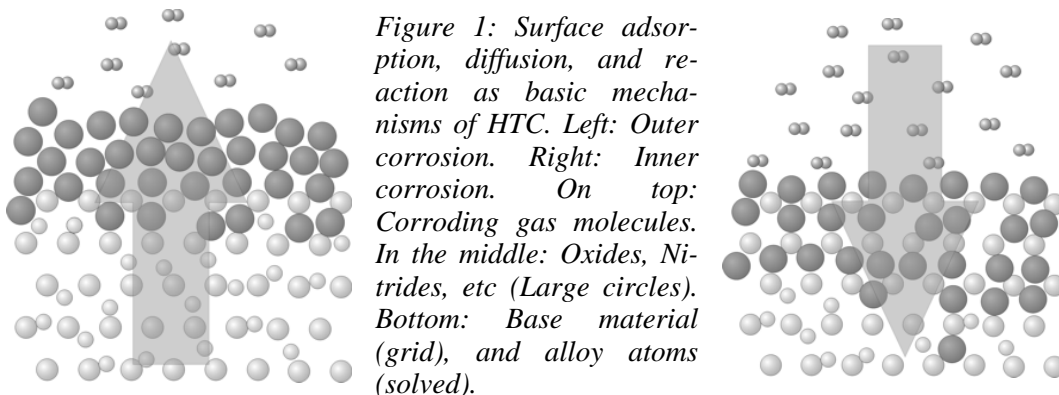
Figure 1: Surface adsorption, diffusion, and reaction as basic mechanisms of HTC. Left: Outer corrosion. Right: Inner corrosion. On top: Corroding gas molecules. In the middle: Oxides, Nitrides, etc (Large circles). Bottom: Base material (grid), and alloy atoms (solved).

1. They immediately react with alloy components at the surface (outer oxidation). Coating oxide layers are formed that separate the base material form the surrounding atmosphere and so prevent further oxidation.

2. If the oxide layer is damaged or weak, gas atoms can diffuse into the base metal to form precipitations of oxide, nitride, etc. (inner oxidation). The resulting damage caused by the change of the material microstructure is extremely dangerous because it cannot be diagnosed by inspection of the metal surface.

During the life time of a high temperature material both processes take place: The oxide layer breaks due to mechanical stresses and corroding gas diffuses into the base material until, finally, the oxide layer closes again. The speed of this self healing process is determined by the diffusion of alloy components in the base material. The whole process takes place as long as there are still enough alloy components available. Afterwards, catastrophic corrosion will occur very rapidly which must be prevented by all means.

Because this will be only the case after several years, simulation tools are required to predict the life time of high temperature materials. Of special interest is the influence of different corroding atmospheres on different alloy compositions, the interplay between outer and inner corrosion, the influence of the material structure (e.g. grain boundaries) and the investigation of complex three-dimensional geometries. Efficient simulation tools are required to obtain practically useful results in reasonable computing time.

A computational engine for HTC processes has been implemented that facilitates simulation studies on a mesoscopic scale. Mesoscopic here means a spatial resolution well above the atomistic scale. On the other hand, spatial structures like oxide layers, grain boundaries or precipitations should be resolvable [5]. Because the available reaction kinetic knowledge is rather rough (see below) and very long time periods have to be simulated the main emphasis is on the speed of simulation.

2 Modeling HTC Processes

HTC processes on the meso scale are described by reaction diffusion systems

$$\dot{u}_i = \nabla \left[D_i \nabla u_i \right] + F_i(u_1, \ldots, u_n), \quad i = 1, \ldots, n \tag{1}$$

where the spatially distributed variables u_i denote the concentrations of different chemical substances diffusing in the matrix of the base metal. The respective diffusion coefficients D_i can be zero in case of immobile oxides or nitrides. The main problem with Equation (1) is that the reaction term $F(u_1, \ldots, u_n)$ is not precisely known in practice. Instead the following knowledge can be used for modeling [2,6]:

1. High temperature corrosion processes are typically diffusion limited, i.e. the reactions are much faster than the diffusion processes.

2. Under the condition that no diffusion is present the thermodynamic equilibrium

$$u_i^* = u_i^*(u_1, \ldots, u_n), \quad i = 1, \ldots, n$$

   of the reaction can be computed from a Gibbs energy minimization [3].

Gibb's energy minimization relies on an empirical model of the free Gibb's energy:

$$G = G(\vec{u}) \qquad \vec{u} = \left(u_1, u_2, ..., u_n\right)^T \qquad (2)$$

which is approximated in terms of complex mixed logarithmic/polynomial models. The coefficients of these models are taken from calorimetric experiments and stored in data bases [3]. Using this empirical Gibb's energy model the determination of the thermodynamic equilibrium ends up with a minimization problem:

$$\vec{u}^* = \underset{\mathbf{S} \cdot \vec{u} = \mathbf{S} \cdot \vec{u}_0 \quad \vec{u} \geq \vec{0}}{\arg \min} G(\vec{u}) \qquad (3)$$

Here $\vec{u}_0$ is the vector of initial concentrations and $\mathbf{S}$ is the stoichiometric matrix of the reaction system. Highly sophisticated thermodynamic computation tools are available to solve this problem [3]. Knowing this computational building block, two kinds of approximations can be used to model HTC with a reasonable precision:

Quasi-Stationary approach: The time-continuous process is discretized as a series of diffusion steps and reaction equilibria computations:

$$\begin{aligned}
\dot{u}_i(\tau) &= \nabla\left[D_i \nabla u_i(\tau)\right], \quad t < \tau < t + \Delta t \\
u_i(\tau) &:= u_i^*(u_i(\tau)), \qquad \tau = t + \Delta t
\end{aligned} \qquad (4)$$

This means that the alloy compounds are allowed to diffuse freely without any reaction for some small time step Δt. Then all concentrations are forced to their local reaction equilibria. Although this method is widely used [4,6], its methodological drawback is that a simulation parameter Δt is mixed up with physically meaningful parameters.

Pseudo-Kinetic approach: "Pseudo reaction kinetic" terms $F_i(u_1, ..., u_n)$ are constructed from the known chemical equilibrium and the current concentration. In each case phenomenological velocity constants k must be introduced to determine the time scales of the reactions. There are different ways to do this:

1. A "driving force" towards the equilibrium is introduced:

$$F_i(u_1, ..., u_n) = -k_i \cdot (u_i - u_i^*), \quad i = 1, ..., n \qquad (5)$$

2. The projection of the Free Gibb's energy gradient to the stoichiometric space is used:

$$\vec{F}(\vec{u}) = -k \cdot \mathbf{P} \cdot \nabla G(\vec{u}), \quad \mathbf{P} = \mathbf{1} - \mathbf{S}^T (\mathbf{S} \cdot \mathbf{S}^T)^{-1} \mathbf{S} \qquad (6)$$

3. As an extension of the second approach the projected gradient is scaled with the energy difference between current and equilibrium state:

$$\vec{F}(\vec{u}) = -k \cdot (G(\vec{u}) - G(\vec{u}^*)) \cdot \frac{\mathbf{P} \cdot \nabla G(\vec{u})}{\left\|\mathbf{P} \cdot \nabla G(\vec{u})\right\|} \qquad (7)$$

Equation (6) basically implements a gradient based optimization algorithm as a part of the reaction diffusion equations at the risk of becoming trapped in local optima. Likewise, Equation (7) becomes singular at an energy minimum and thus must be appropriately stabilized (e.g. by mixing (6) and (7)). Thus, in general the quasi-stationary approach (4) and the pseudo-kinetic variant (5) will be most robust. For brevity only these two approaches are considered in the following.

3 Computational Tools

From a computational viewpoint the numerical solution of the diffusion reaction system (1) first requires the solution of a diffusion equation (usually in two or three dimensions). This can be efficiently managed with standard discretization schemes for diffusion equations (e.g. Crank-Nicholson, Finite Elements) but also with modern adaptive schemes.

Secondly, a thermodynamic equilibrium calculation (3) has to be done for every point of the computational grid and every time step of the PDE solver. This equilibrium computations consume the vast majority of HTC simulation time. Consequently, the numerical solution of problem (3) must be accelerated to speed up the whole simulation. Unfortunately, the details of the thermodynamic calculations are hidden in the commercial thermodynamic software which must be treated as a black box.
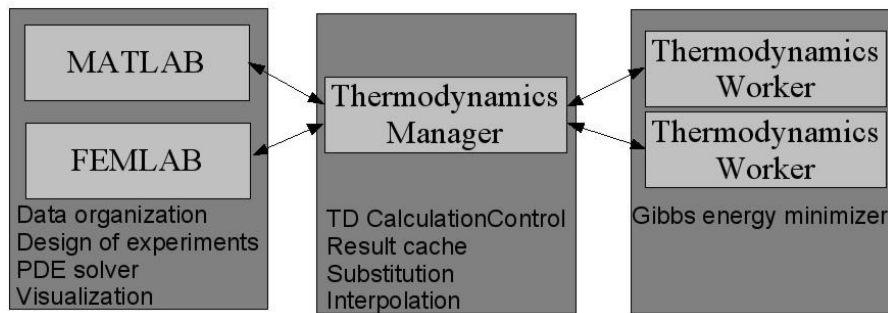

Figure 2: Architecture of the computational engine.

For this reason a thermodynamics manager has been implemented which accelerates the calculations by two measures (Figure 2):

1. For every time step of the PDE solver the thermodynamic calculations on the computational grid are independent from each other and thus can be distributed on a compute cluster. PVM has been used in the present implementation for task distribution.

2. All results already computed by the Gibbs energy minimization routine are stored in an interpolation table. New computations are only triggered, if the required information cannot be already interpolated with good precision from this table. A simple interpolation scheme turned out to be sufficient. It operates with two distance thresholds $\lambda_{lo} < \lambda_{hi}$:

   a. If the distance between the lookup vector $\vec{u}$ and some vector $\vec{u}_i$ stored in the table is smaller than λ_{lo}, the already computed equilibrium value $\vec{u}_i^{*}$ is returned.

   b. If the nearest neighbor of $\vec{u}$ is in a distance between the thresholds a linear regression interpolation is computed by taking all values $\vec{u}_{i_1}, \vec{u}_{i_2}, ..., \vec{u}_{i_k}$ in this neighborhood.

   c. If the distance is above both thresholds a new computation is triggered.

It is important to project every interpolated value to the stoichiometric subspace before using it (see Equation (8)). The reason is that without this projection the molar mass balances would not be closed, thus leading to simulation artifacts. A special but rare case occurs, when the stoichiometric projection leads to negative concentrations. In this case the restricted optimization problem of type

$$\vec{u}_S^{\;*} = \underset{\mathbf{S}\cdot\vec{u}_S = \mathbf{S}\cdot\vec{u}_0 \quad \vec{u}_S \geq \vec{0}}{\arg\min} \left\| \vec{u}_S - \vec{u}^* \right\|^2 \tag{8}$$

has to be solved where $\vec{u}^*$ is the interpolated value. If the inequality is not violated this is exactly the projection to the stoichiometric space.
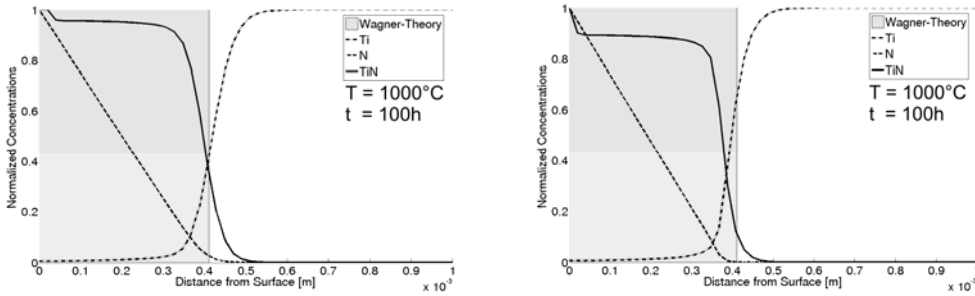

Figure 3: Comparison of simulation results with the 1-dimensional Wagner theory for a nickel-titanium alloy with nitrogen as corroding gas. For time t=100h Wagner theory predicts a sharp nitride front (shaded). Left: Quasi-stationary approach (4) with a moderate step size Δt. Right: Pseudo-kinetic approach (5) with moderate kinetic constants k_i.

4   Comparing the Modeling Approaches

In a simple 1-dimensional situation an analytical situation for Equation (1) based on the classical Wagner corrosion theory is available [2]. This theory is restricted to systems with 3 components (gas, alloy, base metal) with zero initial gas concentration. Moreover, the reacting alloy must never be exhausted and the reaction equilibrium must be instantaneously reached. This corresponds to the limit $\Delta t \rightarrow 0$ in the quasi-stationary Equations (4).

For a Wagnerian system the different modeling approaches have been compared (Figure 3). As expected, both the quasi-stationary and the pseudo-kinetic approach converge to the ideal Wagner solution for $\Delta t \rightarrow 0$ or $k \rightarrow \infty$, respectively. Clearly, close to the limit, the computation time for the quasi-stationary approach tends to infinity whereas the pseudo-kinetic equations become more and more stiff and thus cause a high computational effort of the PDE solver. Notice, that the reaction front is well reproduced even with moderate values of ΔT or k (Fig. 3). This shows that, in practice, the precise knowledge of these constants is not relevant and simulation time can be significantly reduced by taking moderate values.

5   Complex Simulation Example

As a more realistic example the oxidation along grain boundaries is presented. In the considered corrosion system a boiler steel with a low chromium content is exposed to air at 550 °C. It is assumed that diffusion along grain boundaries is more rapid than inside the grains. For simplicity the grain structure is modeled in 2 dimensions by a rectangular grid. A standard Finite Difference scheme can then be used to discretize Equations (1). and the Crank-Nicholson time-stepping scheme was used for numerically stable solution of the arising ODE system in MATLAB. Figure (4) shows the simulation results for one of the formed oxidation products (Fe_3O_4).
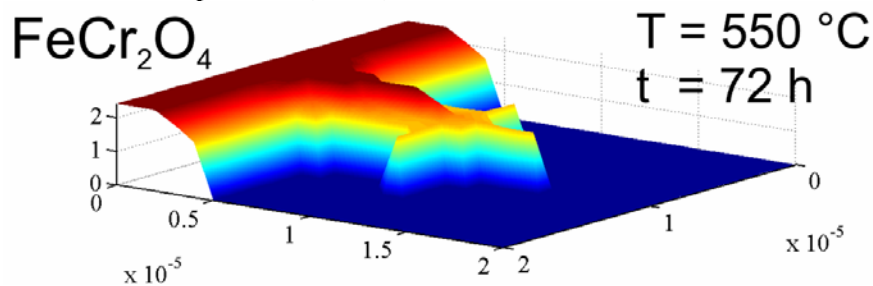

Figure 4: Example of a grain boundary diffusion and oxidation process. Left boundary: Metal surface. Obviously, oxidation prefers the grain boundaries.

For this system the simulation time was 72 h. From a total of $1.3 \cdot 10^6$ possible Gibb's energy minimizations only approx. 200 had to be really executed. In general it turned out that with the new approach that the computation time for meso scale simulations is reduced by several orders of magnitude. In fact the interpolation table remains surprisingly small in most practical applications. The reason is that the reaction typically takes place at a sharp reaction front whereas over wide ranges of the material there is only diffusion taking place (Figures 3,4). Because the reaction front looks similar over the whole time (although it might move) the interpolation table needs only a few values to describe every possible situation.

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