HYDRIDE NUCLEATION - GROWTH - DISSOLUTION MODEL:
IMPLEMENTATION IN BISON

A Thesis in
Nuclear Engineering
by
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Abstract

During the operation of a light water reactor, a fraction of the hydrogen produced by waterside corrosion is absorbed into the nuclear fuel cladding. When the hydrogen concentration reaches the solubility limit, a brittle zirconium hydride phase precipitates in the cladding, leading to a loss of ductility. To assess cladding integrity, an accurate simulation tool is needed to predict hydrogen distribution within the cladding and hydride precipitation. Such a model has been introduced into the fuel performance code BISON, developed at Idaho National Laboratory. However, recent studies have developed a more accurate understanding of the physical processes involved in hydride precipitation and dissolution. In this work the Hydride Nucleation-Growth-Dissolution (HNGD) model was implemented into BISON. Each step of the development was carefully verified. Validation simulations show that the HNGD model captures some experimentally observed physical phenomena that the previous model did not, especially during fast thermal transients.
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CHAPTER 1
Introduction to the Hydride Problem

The temperature, pressure and radiation conditions in a nuclear reactor create a challenging environment for the materials in the core. Zirconium alloys were chosen as nuclear fuel cladding material because they present many advantages. In addition to good mechanical properties, thermal conductivity and corrosion resistance, Zirconium is also almost transparent to neutrons. Moreover, its behavior under radiation is acceptable as it is resistant to void swelling. Two main issues can arise: creep and growth because of the anisotropy of the crystal structure, and the corrosion hydriding occurring during operation. [1]

Once an oxide layer is formed on the surface of the metal, it isolates the cladding from the water so the oxidation reaction described in Equation 1.1 requires additional steps to be completed.

\[
Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 \quad (1.1)
\]

This process is illustrated in Figure 1.1: oxygen ions have to diffuse through the oxide layer to react with the zirconium, producing the oxide. There are two possibilities to complete the reaction. The electrons produced by the oxidation can be transported through the oxide and react with protons to form \( H \) molecules dissolved in water, or protons can diffuse through the oxide and be absorbed by the Zircaloy [2]. These two phenomena can happen in parallel, and their respective kinetics determines the corrosion rate and the hydrogen pick-up fraction. This
fraction can be expressed as

\[ f = \frac{H_{\text{absorbed}}}{H_{\text{produced}}} \quad (1.2) \]

where \( H_{\text{produced}} \) is the amount of hydrogen produced by the corrosion reaction (Eq. 1.1) and \( H_{\text{absorbed}} \) is the amount of hydrogen that diffuses through the oxide layer and gets absorbed by the cladding.

Once hydrogen has entered the cladding, it can redistribute under the concentration and temperature gradients. Figure 1.2 shows the two components of the hydrogen diffusion described by Equation 1.3:

\[ \frac{\partial C_{SS}}{\partial t} = - \nabla \left( - D \nabla C_{SS} - \frac{Q^* C_{SS}}{RT^2} \nabla T \right) \quad (1.3) \]

where \( C_{SS} \) is the concentration of hydrogen in solid solution, \( D \) is the diffusion coefficient of hydrogen in zirconium (following an Arrhenius law), \( Q^* \) is the heat of transport of hydrogen in zirconium (assumed constant) and \( R \) the ideal gas constant. The first term, proportional to the hydrogen concentration gradient, is Fick’s law. This component tends to homogenize the hydrogen content profile. The
Fick’s law that tends to homogenize the distribution, and Soret effect brings the hydrogen to the colder spots.

The second term, proportional to the temperature gradient, is the Soret effect [3] that pushes hydrogen toward the colder parts of the cladding.

When the hydrogen content locally reaches the solubility limit, a zirconium hydride phase precipitates, following the reaction $x Zr + (1 - x)H \rightarrow Zr_x H_{(1-x)}$ [1]. In the cladding, the main temperature gradient is along the radial direction, so the solubility limit is first reached close to the cladding-water interface. However, there are temperature gradients in the axial and azimuthal directions as well. For example the regions between fuel pellets receive less heat, creating gradients along the axial direction. Also, when the thermally insulating oxide layer gets too thick, it can spall off the Zircaloy tube surface. That puts the metal directly in contact with water, creating a cold spot and so an azimuthal gradient. [1]

Zirconium hydrides are brittle, so a high concentration of those particles in the cladding can endanger its integrity. Moreover, the thermo-mechanical history can modify hydride morphology. In particular, an applied stress during cooling causes hydrides to precipitate in the direction perpendicular to the applied stress [1]. Figure 1.3 shows how applying a stress during precipitation changes the disposition of hydride particules. On this picture the vertical direction is equivalent to the radial direction of the cladding. When hydrides precipitate under low stress they precipitate in the horizontal (i.e. circumferential) direction. However, when the applied stress is too high (155 MPa in this case), the majority will precipitate in
Figure 1.3: Hydride reorientation under stress. Stress is applied to an hydrogen-loaded Zircaloy-4 sample with a varying section, showing how the hydride stacking changes depending on the stress [4].

the vertical (i.e. radial) direction. This hydride morphology is more susceptible to failure, as a crack will propagate through the cladding much more easily.

Figure 1.4 summarizes the hydriding process. The hydrogen picked-up during corrosion illustrated in Fig. 1.4a redistributes under concentration and temperature gradients (1.4b). This leads to hydride precipitation with a morphology dependent on the stress (1.4c). The present modeling work focuses on the distribution and precipitation of hydride under no stress.

The model used in this work is called Hydride Nucleation-Growth-Dissolution (HNGD). It takes into account hydrogen diffusion under temperature and concentration gradients (Eq. 1.3), while improving the previous description of zirconium hydride precipitation and dissolution [5].

Before HNGD was developed, the model described by Courty et al. in [6] was used. This model distinguishes 4 cases:

- Precipitation

\[
C_{ss} > TSS_P \Rightarrow \begin{cases} 
\frac{dC_{ss}}{dt} = -\nabla J - \alpha^2(C_{ss} - TSS_P) \\
\frac{dC_{prec}}{dt} = \alpha^2(C_{ss} - TSS_P) 
\end{cases}
\] (1.4)

where \( J \) is the hydrogen flux, \( \alpha^2 \) is a kinetic coefficient, and \( TSS_P \) is the Terminal Solid Solubility for Precipitation, following an Arrhenius law. If
Figure 1.4: Schematic summarizing the hydriding process. Water side corrosion of the Zircaloy causes hydrogen absorption. This hydrogen is distributed by Fick’s law and Soret effect, and a high hydrogen content lead to zirconium hydride precipitation with a morphology depending on the applied stress.

The concentration of hydrogen in solid solution exceeds the $TSS_P$ value then there is precipitation of hydrides.

- **Dissolution**

  \[
  \begin{cases}
  C_{ss} < TSS_D \\
  C_{prec} > 0
  \end{cases}
  \Rightarrow
  \begin{cases}
  \frac{dC_{ss}}{dt} = -\nabla J - \beta^2 (C_{ss} - TSS_P) \\
  \frac{dC_{prec}}{dt} = \beta^2 (C_{ss} - TSS_P)
  \end{cases}
  \quad (1.5)
  \]

  where $TSS_D$ is the Terminal Solid Solubility for Dissolution and $\beta^2$ is a kinetic factor. If the concentration of hydrogen in solid solution is below the $TSS_D$ and there are hydrides in the matrix, then these hydrides dissolve.

- **Hysteresis**

  \[
  TSS_P \geq C_{ss} > TSS_D \Rightarrow
  \begin{cases}
  \frac{dC_{ss}}{dt} = -\nabla J \\
  \frac{dC_{prec}}{dt} = 0
  \end{cases}
  \quad (1.6)
  \]

  If the concentration of hydrogen in solid solution is between the $TSS_P$ and $TSS_D$ curves then no precipitation or dissolution is occurring.
• **Diffusion only**

\[
\begin{align*}
C_{ss} < TSS_D \
C_{prec} = 0 \Rightarrow \begin{cases}
dC_{ss}/dt = -\nabla J \\
dC_{prec}/dt = 0
\end{cases}
\end{align*}
\]

(1.7)

If all hydrogen is in solid solution with a concentration lower than \((TSS_D)\) then no precipitation or dissolution occurs, the hydrogen is only submitted to diffusion under temperature and concentration gradients.

This understanding came from experiments showing the behavior illustrated in Figure 1.5. If a hydrogen-loaded sample of Zircaloy it heated up, from 300K to 800K in the case of Figure 1.5a, i.e. dissolving hydride particles, the solid solution concentration follows the \(TSS_D\) curve. However, when the sample is cooled down once all hydride are dissolved, precipitation will happen when the solid solution concentration reaches the \(TSS_P\) value.

But more recent experiments showed that hydride precipitation actually occurs

![Figure 1.5: Illustration of the hysteresis considered in the previous model. Considering a heat-up from 300K to 800K, the hydrides dissolves in such a way that the concentration of hydrogen in solid solution follows the \(TSS_D\) curve (a). When the Zircaloy is cooled down from 800K (b), the hydrides precipitate when the solid solution content reaches \(TSS_P\). From there the solid solution content follows the \(TSS_P\) curve.](image)
Figure 1.6: Illustration of the hydride content evolution in a sample that is cooled down (a) and then maintained at a fixed temperature (b). Precipitation continues at a slow rate, around 50wt.ppm/h in the experiments shown in [7].

under $TSS_P$ if hydrides are already present in the sample [7]. This precipitation takes hours to be noticeable, and is attributed to hydride growth, while the faster precipitation that follows $TSS_P$ is attributed to new hydride nucleation. So $TSS_P$ is actually the thermodynamic equilibrium solubility, whereas $TSS_D$ is the supersaturation allowed in the matrix before hydride particles start to nucleate.

The two models and their differences are illustrated in 1.7. The hysteresis when no dissolution or precipitation can occur considered in the previous model (1.7a) does not exist in the HNGD model. Growth can occur anywhere above the solubility limit as long as there are hydrides in the matrix, nucleation occurs when the solid solution content reaches the supersolubility, and hydrides dissolve if they exist in a undersaturated Zircaloy matrix. Moreover, nucleation growth and dissolution each has its own kinetic parameter. These three phenomena are described by Equations 1.8 to 1.10:

\[
Dissolution : \frac{\partial C_{SS}}{\partial t} = -K_D(C_{SS} - TSS_D)
\]  

(1.8)
Figure 1.7: Illustration of the HNGD model (b), compared with the previous model (a). The hydrogen behavior is determined by the temperature and hydrogen solid solution content conditions. The previous model considers that precipitation occurs when the solid solution content is above the $TSS_P$ curve, dissolution happens under the $TSS_D$ curve, and that there is an hysteresis where nothing happens between these two limits. This hysteresis does not exist in the HNGD model, and precipitation can occur via nucleation and/or growth. Moreover, hydride dissolution is no longer considered instantaneous.
Nucleation: \( \frac{\partial C_{SS}}{\partial t} = -K_N (C_{SS} - TSS_P) \) 

\( \) \hfill (1.9) \hfill 

Growth: \( \frac{\partial C_{SS}}{\partial t} = -K_G (C_{tot} - TSS_D).p.(1 - x)(-\ln(1 - x))^{1-1/p} \) 

\( \) \hfill (1.10) \hfill 

where \( C_{SS} \) is the solid solution content of hydrogen, \( C_{prec} \) is the concentration of hydrogen as precipitated hydrides, \( C_{tot} = C_{SS} + C_{prec} \) is the total hydrogen content, \( K_D, K_N, K_G \) are the respective kinetic parameters for dissolution, nucleation and growth, \( x = \frac{C_{tot} - C_{SS}}{C_{tot} - TSS_D} \) is a measure of the advancement of the precipitation reaction, and \( p \) is the dimensionality of the growth (\(~2.5\) for platelets) according to the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model. [8].

In the cladding, hydrogen in solid solution is subject to Fick’s law (driven by concentration gradient) and to the Soret effect (driven by temperature gradient). These two effects affect the hydrogen concentration in solid solution as per Equation 1.3:

In this work is detailed the implementation of the HNGD model. First the model is developed as a stand-alone version, and carefully verified and validated. Then HNGD is implemented into BISON, a finite element based nuclear fuel performance code developed at INL [9]. Again, each phenomenon is verified, and the model predictions are compared with experimental data.
CHAPTER 2
Development of a C++ stand-alone version of the HNGD model

Before starting to update a software such as BISON, the first step is to develop a stand-alone C++ version of the HNGD model. This is done in order to allow individual verification of each phenomenon, and to allow easier debugging than if HNGD is directly coupled to other BISON models. This chapter explains the development steps. The complete code can be found on a public GitHub repository (Appendix A)

2.1 Code Structure and Parameters

This HNGD code simulates hydrogen behavior in a 1D geometry, using an explicit finite difference scheme (Euler method). This type of method requires quite small time steps, and as a result it can have a higher computational cost than its implicit version but it is also simpler to implement, and the long term objective is to use BISON that uses an implicit scheme.

This version of the HNGD model is contained in three files: MainProgram.C, HydrogenBehaviorModel.C and HydrogenBehaviorModel.h. The first manages the input/output files reading and writing, and the simulation time loop. This loop uses an instance of the HydrogenBehaviorModel class that contains the methods used to solve the equations. The main method of this class is computeProperties(),
and it uses auxiliary functions to compute the various values it needs (solubility, kinetics, diffusion flux...). The complete code is available on a GitHub repository (Appendix A).

To maximize flexibility, the model parameters are provided in input files. The first file contains the computation settings (which phenomena to simulate, spatial discretization, time step, etc). The second file contains the temperature history to be used in the simulation, provided in three columns, which specify respectively specify the time (s), the average temperature (K) and the temperature gradient (K/cm). The average temperature and gradient are linearly interpolated between the provided time values. The final input file provides with the physical parameters (hydrogen content, kinetics, solubility, diffusion). The parameters used in this study come from the original HNGD development [5] [10]. They are are summarized up in Table 2.1 and are further described in the following sections.

Once the equations are implemented, the code needs to be verified and validated. The verification step is the comparison of the results with the analytical solution of a simple case, it is meant to check that the code is mathematically correct. The validation step is the comparison of computed results with experimental data, to check that the code’s predictions are physically correct, i.e. that they correspond to experiments.

## 2.2 Equilibrium computation

The first development step is the computation of the equilibrium state of a homogeneous sample, i.e. computing the equilibrium between hydrogen in solid solution and hydrogen in hydride particles, depending on the solubility and supersolubility values. These two parameters follow Arrhenius laws given in Equation 2.1:
Table 2.1: Default parameters of the HNGD model \[5\] \[10\]

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<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
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<td>$E_{th2}$</td>
<td>$2 \times 10^{-7} \text{eV.at}^{-1}\cdot\text{K}^{-2}$</td>
</tr>
<tr>
<td></td>
<td>$E_{th3}$</td>
<td>$3 \times 10^{-10} \text{eV.at}^{-1}\cdot\text{K}^{-3}$</td>
</tr>
<tr>
<td>Activation energy of the diffusion-controlled growth kinetics Arrhenius laws (Eq. 1.10)</td>
<td>$E_G$</td>
<td>0.9 \text{eV.at}^{-1}</td>
</tr>
<tr>
<td>Heat of transport of hydrogen in zirconium.</td>
<td>$Q^*$</td>
<td>25500 \text{J.mol}^{-1}</td>
</tr>
</tbody>
</table>

$$
TSS_D = TSS_D^0 \cdot \exp \left( \frac{-Q_D}{RT} \right) \\
TSS_P = TSS_P^0 \cdot \exp \left( \frac{-Q_P}{RT} \right)
$$

(2.1)

where the pre-exponential factors $TSS_D^0$, $TSS_P^0$ and activation energies $Q_D$, $Q_P$ are fitted to the experimental data from the literature (\[11–16\]). At this point, only hydride nucleation and dissolution are taken into account. Equations 1.8 and 1.9 show that the respective equilibrium states for dissolution and nucleation are $TSS_D$ and $TSS_P$.

Figure 2.1a shows the computation of the equilibrium hydrogen concentration when taking into account only these two phenomena (no hydride growth). The temperature (right vertical axis) starts at 800 K so all hydrogen is in solid solution. From there it decreases linearly with time to 300 K, causing hydride precipitation.
Figure 2.1: Verification of Nucleation-Dissolution equilibrium computation (a) and Nucleation-Growth-Dissolution equilibrium computation (b). On the first plot the nucleation equilibrium is $TSS_p$ and the dissolution one is $TSS_d$. This mimics the equilibrium of the previous model. On the second plot, precipitation also occurs when the supersolubility falls below the solid solution content, but the equilibrium is the solubility value because of growth.
via nucleation, then increases back to 800 K, causing dissolution of the hydrides. The concentration of hydrogen in solid solution (left axis) follows the $TSS_P$ curve during precipitation, and $TSS_D$ during dissolution, which mimics the equilibrium states described by the previous model [6]. When hydride growth computation is added to an otherwise identical simulation case, the equilibrium value for the precipitation is the solubility limit (Fig. 2.1b). That is, the concentration of hydrogen falls to $TSS_D$ as soon as it would reach $TSS_P$, and continues to follow the solubility curve until complete dissolution of all the hydrides particles.

So we are able to compute the equilibrium of hydrogen between solid solution and hydride particles in a homogeneous hydrogen-loaded sample, with or without hydride growth. Next step is the implementation of the kinetics of hydride nucleation, growth and dissolution.

2.3 Kinetics implementation

In the HNGD model the dissolution and nucleation kinetic parameters follow an Arrhenius-type law. Hydride growth can be limited by two factors: diffusion and reaction. Nucleation and growth kinetic factors also depend on the hydride content. These three factors are described in Equations 2.2 to 2.4. [5] [10]

\[
Dissolution : K_D = K_{D0} \cdot e^{(-\frac{E_D}{RT})}
\]

\[
Nucleation : K_N = K_{N0} \cdot f_\alpha \cdot \chi \cdot e^{(-\frac{E_{th}}{RT})}
\]

\[
Diffusion \ controlled : K_{diff} = K_{diff0} \cdot f_\alpha \cdot v_0 \cdot e^{(-\frac{E_G}{RT})}
\]

\[
Reaction \ controlled : K_{th} = K_{th0} \cdot f_\alpha \cdot v_0 \cdot e^{(-\frac{E_{th}}{RT})}
\]

\[
Growth : K_G = \left( \frac{1}{K_{diff}} + \frac{1}{K_{th}} \right)^{-1}
\]
where $K_{D0}$, $K_{N0}$, $K_{dif0}$, $K_{th0}$ are the preexponential factors of the Arrhenius laws for dissolution, nucleation, diffusion-controlled growth, and reaction-controlled growth; $E_D$ is the activation energy for diffusion; $E_G$ is the activation energy for growth by diffusion, and $E_{th}$ is the hydride formation energy, fitted with a third degree polynomial (Equation 2.5).

$$E_{th} = -E_{th0} + E_{th1}.T - E_{th2}.T^2 + E_{th3}.T^3$$ (2.5)

where $E_{th0}$, $E_{th1}$, $E_{th2}$ and $E_{th3}$ are given in Table 2.1.

The dependencies on hydride content are described by:

- Volume fraction of $\alpha$ phase:

$$f_\alpha = 1 - \frac{x_P}{x_\delta - x_\alpha}$$

- Atomic fraction of hydride (with $M_H$ and $M_{Zr}$ the atomic weights of hydrogen and zirconium):

$$x_P = \frac{C_{Prec}}{M_H \cdot \left(\frac{C_{Prec}}{M_H} + \frac{10^9-C_{Prec}}{M_{Zr}}\right)}$$

- Atomic fraction of hydrogen at the ($\delta/\alpha + \delta$) boundary [10]:

$$x_\delta(T) \approx -9.93 \times 10^{-11}.T^3 + 8.48 \times 10^{-8}.T^2 - 5.73 \times 10^{-5}.T + 0.623$$

- Atomic fraction of hydrogen in the $\alpha$ phase:

$$v_0 = \frac{x_0 - x_\alpha}{x_\delta - x_\alpha}$$

- Atomic fraction of hydrogen (total):

$$x_0 = \frac{C_{tot}}{M_H \cdot \left(\frac{C_{tot}}{M_H} + \frac{10^9-C_{tot}}{M_{Zr}}\right)}$$
Atomic fraction of hydrogen in the $\alpha$ phase:

$$x_{\alpha} = \frac{TSS_D}{M_H \cdot \left(\frac{TSS_D}{M_H} + \frac{10^6 - TSS_D}{M_Zr}\right)}$$

$\chi$ is defined as:

$$\chi = \frac{17000 - C_{Prec}}{17000}$$

The computation of the kinetic factors is added to the $HydrogenBehaviorModel$ class, in the $computePhysicalParameters()$ function that also computes the solubility and supersolubility. A new parameter is added into the settings input file to choose between kinetic or equilibrium computation.

Once the code is able to compute the kinetic factors, each phenomenon must be verified individually. These steps are detailed in the next subsections.

### 2.3.1 Dissolution Verification

The hydride dissolution verification case assumes a sample loaded with $C_{\text{tot}} = 540$ $wt.$ ppm of hydrogen at a constant temperature $T = 700$ $K$. At this temperature, the equilibrium concentration of hydrogen in solid solution is $TSS_{700}^D = 230$ $wt.$ ppm. Using the initial condition $C_{SS}(t = 0) = 0$ $wt.$ ppm (all hydrogen is contained in the hydride particles) the analytical solution is given by Equation 2.6:

$$C_{SS}(t) = TSS_{700}^D \left(1 - e^{-K_{700}^D t}\right)$$  \hspace{1cm} (2.6)

with $K_{700}^D = 0.54$ $s^{-1}$. Figure 2.2 shows a plot of the calculated evolution of the solid solution hydrogen content over time for several time step values, compared to the analytical solution. As the time step is reduced, the numerical solution converges to the analytical solution, to the point where the simulation and the solution merge. As expected, this convergence happens when the time step $dt$ is much smaller than the time constant: $1/K_D = 1.8$ s $>> dt \approx 10^{-2}$ s.
Figure 2.2: Dissolution verification: Simulation at constant temperature, starting with a 0 wt.ppm solid solution content. In this simple case the analytical solution is an exponential evolution. When the time step is reduced the result converges to the analytical solution.

### 2.3.2 Nucleation Verification

The nucleation verification case assumes a sample loaded with $C_{tot} = 540$ wt.ppm of hydrogen at a constant temperature $T = 600$ K. At this temperature, the equilibrium concentration of hydrogen in solid solution, when considering hydride nucleation only, is $TSS_{600} = 195.5$ wt.ppm. Moreover, we introduce an approximation on the nucleation kinetic: the kinetic factor is made to follow a pure Arrhenius law by forcing $f_α = χ = 1$. This assumption is not physical, but it makes it possible to derive an analytical solution. At constant temperature and starting with all hydrogen in solid solution ($C_{SS}(t = 0) = 541$ wt.ppm) the analytical solution is given by Equation 2.7. In this calculation, the growth computation is disabled so only hydride nucleation can modify the hydrogen content in solid solution.
Figure 2.3: Nucleation verification: Simulation at constant temperature, starting with all hydrogen in solid solution. In this simple case (the dependencies of the kinetic parameter on hydride content is ignored) the analytical solution is a simple exponential solution. When the time step is reduced the result converges to the analytical solution.

\[ C_{SS}(t) = TSS_P + (C_{tot} - TSS_P)e^{-K_N^{600} \cdot t} \]  

with \( K_N^{600} = 1.5 \times 10^{-2} \text{s}^{-1} \). Figure 2.3 shows a plot of the simulated evolution of the hydrogen content in solid solution, computed for several time steps and compared to the analytical solution in red. As in the dissolution verification case, the numerical result converges to the analytical solution when the time step is reduced. The two solutions effectively merge when \( dt.K_N \approx 10^{-2} \).
2.3.3 Growth Verification

The nucleation verification case assume a sample loaded with $C_{tot} = 540\text{ wt.ppm}$ of hydrogen at a constant temperature $T = 653\text{ K}$. At this temperature, the equilibrium concentration of hydrogen in solid solution, when considering hydride nucleation only, is $TSS^6_{D} = 295\text{ wt.ppm}$. Similarly to what was done in the nucleation verification, the hydride dependency of the hydride growth kinetic factor is ignored verification by forcing $f_\alpha = v_0 = 1$. Moreover, the nucleation computation is deactivated so only hydride growth can modify the hydrogen solid solution concentration. Using a constant temperature ($T = 653\text{ K}$) and considering that all hydrogen is in solid solution in the initial state\(^1\), the advancement $x(t)$ of the $3Zr + 5H \rightarrow Zr_3H_5$ reaction is given by the Avrami equation (Equation 2.8). $x$ is initially 0 and reaches 1 when the reaction is complete, i.e. when the solid solution hydrogen content reaches $TSS_D$.

$$x(t) = \exp\left(-\left(K_G^{653}_G t\right)^p\right)$$

(2.8)

with $K_G^{653} = 2 \times 10^{-4} \text{s}^{-1}$. The coefficient $p$ is the Avrami parameter, representing the dimensionality of the growth, which is $\approx 2.5$ in the case of platelets, and $x$ is computed from the solid solution content: $x = \frac{C_{tot} - C_{SS}}{C_{tot} - TSS^6_D}$ with $TSS^6_D = 295\text{ wt.ppm}$ that is, the reaction is considered complete when $C_{SS} = TSS_D$.

Figure 2.4 shows a plot of the advancement of the reaction for several time step values, compared to the analytical solution. Again the numerical result converges to the analytical solution when the time step is small enough, compared to $1/K_G = 5 \times 10^3\text{s}$.

\(^{1}\text{To force the algorithm to start computing hydride growth, the hydrogen solid solution content must actually be initialized to a non-zero, small value. 10}^{-3}\text{ wt.ppm was used here.}\)
2.3.4 Hydrogen and hydride content dependencies

As mentioned earlier, the dependencies of $K_N$ and $K_G$ on the total hydrogen content and on the hydride content were deactivated by imposing $f_\alpha = v_0 = \chi = 1$ in order to be able to derive analytical solutions. The impact of these factors on kinetics is illustrated in Figure 2.5. These plots show how the kinetic factors of nucleation (Fig. 2.5a) and growth (Fig. 2.5b) are affected by the total hydrogen content (x axis) and the proportion of hydrogen in hydrides (y axis). The $f_\alpha \cdot \chi$ and $f_\alpha \cdot v_0$ products can vary from 0 (the precipitation component cannot occur) to 1 (the kinetic parameter is as high as it gets). At relatively low hydrogen content
\( C_{tot} < 2000 \text{ wt.ppm} \) the nucleation kinetics are barely affected while the growth is almost reduced to zero. It indicates that in these conditions, hydride precipitation occurs mainly through nucleation.

### 2.4 Diffusion implementation

#### 2.4.1 Space discretization

Spatial discretization is achieved by the new function `computeLocations(double X0, double XEnd, double bias, std::vector<double>& x)`. It attributes a position to each of the terms of the \( x \) vector, from \( X0 \) to \( XEnd \). The \( bias \) parameter makes possible to produce a geometry with smaller cells at one end. The function is built such that the spacing between the nodes follows Equation 2.9:

\[
\begin{align*}
  x_1 - x_0 &= \frac{XEnd-X0}{S_{N-1}} \\
  x_{k+1} - x_k &= (x_k - x_{k-1}) \times bias \quad \forall \ k \in [1...N-2] \\
  S_0 &= 1 + bias \\
  S_k &= 1 + bias \times S_{k-1} \quad \forall \ k \in [1...N-2]
\end{align*}
\]

(2.9)

where \( N \) is the number of nodes.

The variables that were until now described by a scalar (temperature, hydrogen contents, kinetic factors, solubility) get a vector equivalent to use when simulating a sample instead of a single cell, and a function is implemented to compute linear profiles for temperature and concentration based on an average value and a gradient.

The `computeProperties()` function is then modified to include a space loop when needed, and a `computePhysicalParameters(int position)` function is added to compute the kinetic factors and solubility values. Figure 2.6 shows that for the same heat treatment the evolution of the concentration of hydrogen in solid solution is the same whether it is computed with or without space discretization, so that consistency is assured when discretization is applied.
Figure 2.5: Dependency of the nucleation (a) and growth (b) kinetic factor on the total and hydride hydrogen content (Eq. 2.3 and 2.4). Nucleation kinetic factor is reduced when increasing the hydrogen content and/or the proportion of this hydrogen in hydrides. Growth kinetic is mainly limited by $C_{tot}$ and is higher when there are few hydrides.
The application of Fick’s law and Soret effect require the computation of several derivatives. For this, a Euler scheme is used:

\[
\frac{\partial f}{\partial x} \bigg|_k = \frac{f_{k+1} - f_k}{x_{k+1} - x_k}
\]

The next step is now to implement the hydrogen diffusion in solid solution.

### 2.4.2 Fick diffusion

The parameters \( D_0 \) and \( E_D \), and an integer parameter to deactivate Fick’s law computation are added to the input files, and the diffusion coefficient computation is added to the `computePhysicalParameters(int position)` function. This coefficient follows an Arrhenius law (Eq. 2.10). The flux computation is implemented in a `computeDiffusionFlux(int position)` function, and `computeProperties()` updates the
solid solution profile.

\[ D = D_0 \exp\left(\frac{-E_D}{RT}\right) \]  

(2.10)

The first verification done for Fick’s law is to check that when starting from a non-homogeneous profile the distribution converges to a flat profile. This is illustrated in Figure 2.7. Here the global hydrogen content is 200 \textit{wt.ppm}, with an initial gradient of 400 \textit{wt.ppm/cm}. The graph shows successive concentration profiles, from blue to green, and indeed the profile which is initially linear becomes flat with increasing time.

However this qualitative verification is not enough, and a situation where an analytical solution is known is needed. For this we use a diffusion couple case, i.e. the concentration is initially zero in a semi infinite sample, except at the origin
where the concentration is maintained at a value $C_0/2$. Using a large sample (10 cm) the analytical solution is given by Equation 2.11.

$$\begin{cases}
C(\infty, t) = 0 \\
C(0, t) = \frac{C_0}{2}
\end{cases} \implies C(x, t) = C_0 \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right)$$

(2.11)

The result of this verification is illustrated in Figure 2.8. Figure 2.8a shows successive concentration profiles. Only the first 2 cm of the sample are shown, because there is little to no hydrogen at longer distance, which justifies the infinite sample approximation. Each computed profile (line) is plotted with its associated analytical profile (points), showing an excellent match. On Figure 2.8b, each curve is the evolution of concentration at position $x = 0.198$ cm for a given discretization size. As the $dx$ is reduced the evolution given by the code converges to the analytical $\text{erfc}$ solution in Equation 2.11 as expected.

### 2.4.3 Soret effect

The second diffusion component is Soret effect, i.e. diffusion driven by a temperature gradient. It requires an additional parameter: the heat of transport of hydrogen in zirconium, noted $Q^*$ and added to the input file. The Soret effect contribution to the diffusion flux is added in the `computeDiffusionFlux(int position)` function.

Again, a simple qualitative verification is possible: if there is no Fickian diffusion to counter Soret effect, all hydrogen should migrate to the coldest cell of the simulation, which is the case, as illustrated in Figure 2.9. The successive profiles, going from blue to green as per the legend, show that the hydrogen concentration drops to 0 everywhere except at the peak that forms at the cold end. This simulation computes only the Soret effect, and no Fick’s law or hydride precipitation are taken into account.

No analytical solution was found for the Soret effect alone, but one can be
Figure 2.8: Verification of Fick’s law computation. In this simulation the analytical solution is given by Eq. 2.11. Figure 2.8a shows the concentration profile on the first 2cm of a 10cm sample at different times. The computed profile (lines) have an excellent agreement with the analytical solutions (dots). The red vertical line indicates the position where the local evolution of solid solution is plotted in Figure 2.8b. Simulations are plotted for different discretization values and compared to the analytical solution; there is a clear convergence of the numerical result to the analytical solution as the cell size decreases.
Figure 2.9: Soret effect computation only: there is no analytical solution for the transient, but without Fickian diffusion all hydrogen should migrate to the cold spot, leaving nothing behind, which is what is observed here with these consecutive content profiles.

derived for the steady state when computing both the Soret effect and Fick’s law (Equation 2.12). The derivation is given in Appendix B.

\[ C_{eq}(x) = C_{eq}(0) \exp \left( \frac{Q^*}{R} \left( \frac{1}{T(x)} - \frac{1}{T(0)} \right) \right) \]  

(2.12)

where \( C_{eq}(x = 0) \) can be calculated numerically using mass conservation (Appendix B). Results for this verification are shown in Figure 2.10. The first plot shows how much time is needed to reach the steady state. In this particular case we take 20000 s. Figure 2.10b shows good agreement between the numerical solution and the analytical solution for different discretizations, each type of marker corresponding to a cell size.
Figure 2.10: Soret and Fick computation: Figure 2.10a shows that there is no noticeable change from 13000 s to 20000 s profiles. 20000 s is used as the steady state result in Figure 2.10b for some spatial discretizations, and the match between the code and this analytical solution is very good.
2.5 Adaptive time step

In order to decrease the computation duration, an adaptive time step is implemented. Its value is updated at every loop, and determined by the fastest phenomenon happening, as shown in Equation 2.13

\[
 dt = \min \left( \frac{dx^2}{2D}, \frac{dx^2}{2D_{\text{Soret}}}, \frac{0.3}{K_D}, \frac{0.3}{K_N}, \frac{0.3}{K_G} \right) \quad \text{with} \quad D_{\text{Soret}} = \frac{D_Q \cdot \nabla T \cdot C_{SS}}{R \cdot T^2} \quad (2.13)
\]

To do so, a spatial loop is needed to determine the phenomena that are actually happening: it would be unnecessary to base the time step value on dissolution kinetics if there is no dissolution happening, for example. The space loop is also made to determine the highest values for \( D \) and \( D_{\text{Soret}} \). The expression \( dt \leq \frac{dx^2}{2D} \) is the convergence criterion, coming from finite difference theory [17]. Once the adaptive time step is implemented a new verification is needed to ensure that the results are not modified. Figure 2.11 shows the hydrogen concentration evolutions in the same cases as in the previous sections, for hydride nucleation (a), dissolution (b) and growth (c). The simulations follow the analytical solutions closely.

2.6 Validation

Several sets of experimental data are available for this code validation, particularly the benchmark cases used by Lacroix during the original development of the HNGD code [5]. Hence the present code can be compared to both experimental data and to the results from the Matlab version. If the same method is used to solve the same equations, the solutions should match.

The first experiment is a series of thermal transients, presented in Figure 2.12. In this case a Zircaloy sample loaded with \(~ 225 \text{ wt.ppm}\) of hydrogen is submitted to a thermal treatment while the global solid solution hydrogen content is monitored.
Figure 2.11: New verification of nucleation (a), dissolution (b) and growth (c) with the adaptive time step. The simulation cases are the same as previously used for verification. The results from the code are in excellent agreement with the analytical solutions. (Note: Not all simulation points were plotted for clarity.)

with X-ray diffraction (diffusion is not of interest here). The temperature changes lead to successive dissolution and precipitation. [5]

Figure 2.12 shows the evolution of hydrogen content in solid solution, comparing the experimental data with BISON using the previous model and the two versions of HNGD code. The previous model in BISON (blue doted line) does not at all follow the experimentally measured hydride content evolution. In contrast, the HNGD model globally follows the concentration variations, and is able to capture behaviors that were previously missed, especially in the 3000s to 8000s interval.
Figure 2.12: Comparison of the present code with experimental data, Lacroix’s version and the model previously used in BISON for the thermal transients experiment [5]. The HNGD model is able to capture precipitation and dissolution physics that BISON could not, and the two HNGD versions match.

The second benchmark for this model is the construction of a Time-Temperature-Transformation (TTT) diagram. The time needed to reach a certain reaction advancement (99% in this case) is plotted with respect to temperature for two hydrogen content values [5]. The simulation result is presented in Figure 2.13, compared with the experimental data and with the result from the Matlab code, and the match between the two codes is excellent.

The third benchmark is an experiment conducted by Sawatzky: a 2.54 cm long hydrogen-loaded Zircaloy sample is submitted to a 137 K/cm temperature gradient ($T_{\text{average}} = 576$ K) for 34 days [18]. The accumulation of hydrogen on the colder side leads to a hydride peak at the separation between a monophasic
Figure 2.13: TTT diagram: Comparison with experiment and Lacroix's version [5], it is a perfect match between the two HNGD codes.

and a biphasic region. Figure 2.14 shows the profile of total hydrogen content for different discretization values. The cell size needs to be small enough for the results to converge. Once this criterion is fulfilled, the present code (lines) shows very good agreement with Lacroix's version (dots), except for a slight downward shift in the monophasic region. For now, no explanation for this difference was found.
Figure 2.14: Comparison of the present code (lines) with Lacroix’s version (dots) for Sawatzky’s experiment [18]. The results in the biphasic region converge to Lacroix’s result when reducing the cell size, but there is a slight downward shift in the monophasic region.

In this chapter we showed the verification and validation processes of the stand-alone HNGD code. It shows very good agreement with Lacroix’s work [10] so the next step is to implement this model into BISON.
CHAPTER 3
BISON Update

BISON is a finite element based nuclear fuel performance code being developed at Idaho National Laboratory (INL). It has the capability to solve thermomechanics coupled with species diffusion and nuclear fuel specific phenomena such as swelling, creep, fission gas product release, and many others [9]. The goal of the implementation of the HNGD model is to use it along the other physics allowed by BISON.

3.1 BISON structure

3.1.1 Computation structure

BISON is based on the open source finite element framework Moose, also developed at INL [19]. As a C++ code it is object-oriented. The details of the finite element method or object-oriented programming are not discussed here: the focus is instead on the C++ classes needed for a model to work, as they will use the Moose framework automatically thanks to inheritance. [9] [19]

For a given system, BISON uses an instance of a Kernel-inherited class for each term of each equation, and these Kernels use Material-inherited classes to compute the parameters they need. Then all Kernels and Materials needed for a model are united in an Action.

In the case of the HNGD model, BISON solves the equations for three variables:
temperature \((T)\), precipitated hydride content \((C_{\text{Prec}})\) and solid solution content \((C_{SS})\) (Eq. 3.1). All terms and their associated Kernels are presented in Table 3.1. With the Material classes associated to each parameter (Table 3.2) they form the HydrideAction. The main task of the BISON update was to modify the HydridePrecipitationRate class in order to account for the new physics brought by the HNGD model.

\[
\begin{align*}
\frac{\partial T}{\partial t} - \alpha.\nabla^2 T &= 0 \\
\frac{\partial C_{\text{Prec}}}{\partial t} &= S \\
\frac{\partial C_{SS}}{\partial t} &= -\nabla(-D\nabla C_{SS} - \frac{DQ^* C_{SS}}{RT^2}.\nabla T) - S
\end{align*}
\] (3.1)

<table>
<thead>
<tr>
<th>Term</th>
<th>Kernel</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\frac{\partial T}{\partial t})</td>
<td>TimeDerivative</td>
</tr>
<tr>
<td>(\frac{\partial C_{\text{Prec}}}{\partial t})</td>
<td>TimeDerivative</td>
</tr>
<tr>
<td>(\frac{\partial C_{SS}}{\partial t})</td>
<td>HydrogenTimeDerivative</td>
</tr>
<tr>
<td>(-\alpha.\nabla^2 T)</td>
<td>CoeffDiffusion</td>
</tr>
<tr>
<td>(\nabla(D\nabla C_{SS}))</td>
<td>IsotropicFlux</td>
</tr>
<tr>
<td>(\nabla(\frac{DQ^* C_{SS}}{RT^2}.\nabla T))</td>
<td>ThermoDiffusion</td>
</tr>
<tr>
<td>(S)</td>
<td>HydrideSource</td>
</tr>
<tr>
<td>(-S)</td>
<td>HydrogenSource</td>
</tr>
</tbody>
</table>
Table 3.2: Parameters and associated Material classes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation rate</td>
<td>$S$</td>
<td><code>HydridePrecipitationRate</code></td>
</tr>
<tr>
<td>Conductivity</td>
<td>$\alpha$</td>
<td><code>HeatConductionMaterial</code></td>
</tr>
<tr>
<td>Diffusivity</td>
<td>$D$</td>
<td><code>ArrheniusMaterialProperty</code></td>
</tr>
<tr>
<td>Heat of transport</td>
<td>$Q^*$</td>
<td><code>GenericConstantMaterial</code></td>
</tr>
<tr>
<td>Solubility</td>
<td>$TSS_D$</td>
<td><code>HydrogenSolubility (new)</code></td>
</tr>
<tr>
<td>Supersolubility</td>
<td>$TSS_P$</td>
<td><code>ArrheniusMaterialProperty</code></td>
</tr>
<tr>
<td>Dissolution kinetic</td>
<td>$K_D$</td>
<td><code>DissolutionKinetics (new)</code></td>
</tr>
<tr>
<td>Nucleation kinetic</td>
<td>$K_N$</td>
<td><code>NucleationKinetics (new)</code></td>
</tr>
<tr>
<td>Growth kinetic</td>
<td>$K_G$</td>
<td><code>GrowthKinetics (new)</code></td>
</tr>
</tbody>
</table>

3.1.2 Software quality

In order to ensure the proper working of BISON, all updates must go through a three-step process. First, to be able to make a merge request the code must comply with formal rules. This is to help ensure that the code is understandable, regardless of who developed it. The input files for verification and validation cases folders must be be added to the test and assessment case respectively. Once the updated code has passed the formal criterion, it has to pass all the test cases implemented before, plus the ones that were created for the update. Finally the code is reviewed by members of the BISON team.
3.2 HNGD implementation

3.2.1 Additional Material classes

In order to maximize flexibility for future simulations (easily adding a zirconium liner for example) the computation of the solubility, supersolubility and nucleation (previously precipitation) kinetic factor were displaced from the \textit{HydridePrecipitationRate} class to new, separate \textit{Material} classes, as well as the dissolution and growth kinetic factors (Table 3.2).

3.2.2 \textit{HydridePrecipitationRate} modification

Two boolean parameters (\_instantaneous\_dissolution and \_compute\_growth) were added to this class so it is still possible to use the previous model.

The temperature and hydrogen content are coupled: the temperature has an effect on the hydrogen through the Soret effect and the solubility limits. To solve systems involving coupled variables, it is useful to compute the partial derivatives of the rate of change of each variable, with respect to the coupled variables. Doing so adds off-diagonal terms to the Jacobian, improving the convergence. All non zero partial derivatives are given in Appendix C.

3.2.3 Verification

The steps to follow here are the same as for the stand-alone version. First the nucleation, growth and dissolution are verified, and it appears that the time step management implemented in BISON sets the time step to values that are too large to get the converged solution (Figure 3.1). When the time step is manually forced to stay under 1\,s the match between the HNGD code and BISON is perfect, but this is not the case when the tolerance is set too high. In all cases however, the steady state BISON approaches is consistent with \textit{TSS}_D. The two input files (one
Figure 3.1: Time step dependency study of hydride nucleation, growth and dissolution: Even though BISON always tend to the correct steady state, the native time step management fails to capture some of the transient behavior. The time step value needs to be manually limited.

for hydride dissolution, the other for precipitation) used here are saved as test cases, and another one is made for the thermal transients benchmark. Figure 3.2 shows the evolution of the hydrogen content in solid solution in this simulation, comparing BISON and the stand-alone code. There are some slight discrepancies at the temperature transitions but the results are almost the same.

The observation of the time-step dependency in the verification cases raises the question of the diffusion time step dependency in previous simulations. Figure 3.3 shows the solid solution content at each end of the sample in the case used for diffusion verification during preliminary work. It appears that there is a time step dependency, but it is not as constraining as it is in the hydride precipitation and dissolution cases so it will not represent a problem for the convergence. A manually-limited time step is also needed when simulating an experiment. Figure
3.4 shows the result of simulations of Sawatzky’s experiment [18]. As previously the time step has to be limited to obtain convergence. The constraint is not as strong as in the verification cases of hydride nucleation, growth and dissolution. This is probably because the Sawatzky simulation starts from an equilibrium state while the verification cases start hundreds of wt.ppm away from \( TSS_D \). However the maximum time step value is still small compared to the experiment duration.

The discretization dependency of the simulations also needs to be addressed, especially for simulations leading to the formation of an hydride peak. It is the case with Kammenzind’s sharp profile experiment: a 2.5 cm hydrogen-loaded (120 wt.ppm) Zircaloy-4 sample is submitted to a 75.1K/cm temperature gradient for 30 days [20]. In Figure 3.5, the left graph shows the convergence of the results when computing the hydride profile for different discretization values, using a
Figure 3.3: Time step dependency of diffusion: the hydrogen content in solid solution is plotted at both ends of the sample with different time step limits (given in seconds), the references are computed with the stand-alone HNGD code. Limiting the time step improves the accuracy, however the maximum value is still an order of magnitude greater than the time step needed for the nucleation-growth-dissolution computation, so it should not be an issue.

uniform cell size, so for an increasing computational cost. On the right graph however, only the bias (as described in Section 2.4.1) changes for a constant number of cells ($N = 40$). This shows that in this kind of case the convergence can be improved without extra computational cost.

### 3.2.4 Validation

The first experiment to be used for validation (and added as assessment case) is Sawatzky’s experiment [18]. Figure 3.6 shows the result from BISON computation compared to the analytical solution, experimental data and result from the previous model [21]. In order to have a first idea of how sensitive to its parameters this model
is, two additional simulations were made with different fitting of the solubility. It is approximated with an Arrhenius law: $TSS_D(T) = TSS_{D0} \cdot e^{-Q_D/RT}$, where $TSS_{D0}$ and $Q_D$ were determined using the various values found in the literature ([11–16]). As a result, these two parameters have a standard deviation associated with each, and Figure 3.6 shows the results obtained using the default solubility, and one standard deviation under and above the default fit. As expected, a lower solubility leads to precipitation further on the right (hotter), causing a shift of the hydride peak to the right. On the other hand, not only the peak is shifted to the left when using a higher solubility, but another accumulation of hydrogen starts to appear at the cold spot. In the case of the first experiment (Fig. 3.6a) it is consistent the experimental data: the first data point is higher than the second one. This tends
Figure 3.5: Discretization dependency in the case of the precipitation peak in Kammenzind’s sharp profile experiment [20]. Figure (a) shows the dependency when using a uniform cell size, Figure (b) shows that using a small amount of cells (40 here), using bias as exposed in Section 2.4.1 makes possible to get a result close to what is obtained with a fine mesh.
to indicate that a very good match with experimental data could be achieved by optimizing the model parameters in their uncertainty ranges.

The same method was used for the simulations of Kammenzind’s experiments, results are presented in Figure 3.6. Kammenzind’s experiments simulations (Figure 3.6) encourage even more the previous statement on parameters optimization, particularly the shallow profile case. Using a one standard deviation range on the solubility, the computation can give a high hydride peak, or little to no precipitation.
Figure 3.6: Comparison of Sawatzky simulations with experimental data and analytical solution from [18]. The simulations ran with three different solubility fits.
Figure 3.6: Comparison of Kamenzind’s sharp (a) and shallow (b) temperature profile experiments simulation with experimental data [20]. The simulations ran with three different solubility fits. The solubility has a dramatic impact on the profile.
CHAPTER 4
Conclusion

The main goal of this work was to develop a verified and validated implementation of the Hydride Nucleation-Growth-Dissolution Model, first as a stand-alone code, and then as part of the INL nuclear fuel performance code BISON.

After analytical verification, the stand-alone version shows excellent agreement with Lacroix’s previous work [10] and offers a reference code for simulations that do not require a temperature profile more complicated than linear.

The implementation in BISON also shows consistent results, and provides additional modeling capabilities, including non-linear temperature profiles and coupling with other BISON models.
APPENDIX A
Stand-alone C++ HNGD model

The stand-alone version can be found on its Github repository. The link and the QR-code can be used to get there. https://github.com/FloPasselaigue/HNGD
APPENDIX B
Diffusion steady state derivation

At steady state, Fick and Soret flux are equal at all positions:

\[ J_{Fick}(x) = -J_{Soret}(x) \]

\[
\frac{dC_{eq}}{dx} = - \frac{Q^* C_{eq} \cdot dT}{R \cdot T(x)^2 \cdot dx}
\]

\[
\frac{C'_{eq}(x)}{C_{eq}(x)} = - \frac{Q^*}{R} \frac{T''(x)}{T(x)^2}
\]

\[
\int_{0}^{x} \frac{C'_{eq}(u)}{C_{eq}(u)} du = \int_{0}^{x} \frac{T'(u)}{T(u)^2} du
\]

\[
\left[ \ln \left( C_{SS}(u) \right) \right]_{0}^{x} = - \frac{Q^*}{R} \left[ - \frac{1}{T(u)} \right]_{0}^{x}
\]

\[
\ln \frac{C_{SS}(x)}{C_{SS}(0)} = - \frac{Q^*}{R} \left( - \frac{1}{T(x)} + \frac{1}{T(0)} \right)
\]

\[
C_{eq}(x) = C_{eq}(0) \exp \left( \frac{Q^*}{R} \left( \frac{1}{T(x)} - \frac{1}{T(0)} \right) \right)
\]
Derivation of $C_{eq}(0)$ using mass conservation:

\[ C_{tot} = \frac{1}{L} \int_0^L C_{eq}(x) dx = \frac{C_{eq}(0)}{L} \int_0^L \exp \left( \frac{-Q^*}{R} \cdot \frac{T(x) - T(x = 0)}{T(x) \cdot T(x = 0)} \right) dx \]

\[ C_{eq}(0) = L \cdot C_{tot} \left[ \int_0^L \exp \left( \frac{-Q^*}{R} \cdot \frac{T(x) - T(x = 0)}{T(x) \cdot T(x = 0)} \right) dx \right]^{-1} \]

\[ C_{eq}(0) \approx \frac{-Q^* \cdot L \cdot C_{tot}}{R} \left[ \sum_{k=0}^{N-2} \frac{T_k - T_0}{T_k \cdot T_0} \cdot (x_{k+1} - x_k) \right]^{-1} \]
APPENDIX C
Partial Derivatives

Non zero partial derivatives are presented here:

Dissolution kinetics:

\[ K_D = K_{D0}.e^{\left(-\frac{E_D}{RT}\right)} \]
\[
\frac{\partial K_D}{\partial T} = \frac{E}{RT^2} + K_{N0X} \cdot \frac{\partial f_\alpha}{\partial T} \cdot e^{-\frac{E_N}{RT}}
\]

Nucleation kinetics:

\[ K_N = K_{N0}f_\alphaX.exp\left(-\frac{E_N}{RT}\right) \]
\[
\frac{\partial K_N}{\partial T} = \frac{E}{RT^2} \cdot K_N + K_{N0X} \cdot \frac{\partial f_\alpha}{\partial T} \cdot e^{-\frac{E_N}{RT}}
\]
\[
\frac{\partial K_N}{\partial C_{Prec}} = K_{N0}(X \cdot \frac{\partial f_\alpha}{\partial C_{Prec}} - \frac{1}{17000} \cdot f_\alpha) \cdot e^{-\frac{E_N}{RT}}
\]

Growth kinetics:

\[ K_G = \left(\frac{1}{K_{th} + \frac{1}{K_{mob}}}\right)^{-1} \]
\[
\frac{\partial K_G}{\partial T} = K_G^2 \left(\frac{1}{K_{th}^2 \frac{\partial T}{K_{th}}} + \frac{1}{K_{mob}^2 \frac{\partial T}{K_{mob}}}\right)
\]
\[
\frac{\partial K_G}{\partial C_{Prec}} = -K_G^2 \left(\frac{1}{K_{th}^2 \frac{\partial C_{Prec}}{K_{th}}} + \frac{1}{K_{mob}^2 \frac{\partial C_{Prec}}{K_{mob}}}\right)
\]
\[
\frac{\partial K_G}{\partial C_{SS}} = -K_G^2 \left(\frac{1}{K_{th}^2 \frac{\partial C_{SS}}{K_{th}}} + \frac{1}{K_{mob}^2 \frac{\partial C_{SS}}{K_{mob}}}\right)
\]
Diffusion and reaction driven components:

\[ K_i = K_{i0} \cdot f_\alpha \cdot v_0 \cdot \exp\left(\frac{-E_i}{RT}\right) \]

\[ \frac{\partial K_i}{\partial T} = \frac{E_i}{RT^2} \cdot K_i + K_{i0} \cdot (\frac{\partial v_0}{\partial T} \cdot f_\alpha + v_0 \cdot \frac{\partial f_\alpha}{\partial T}) \cdot \exp\left(\frac{-E_i}{RT}\right) \]

\[ \frac{\partial K_i}{\partial C_{\text{Prec}}} = K_{i0} \cdot (\frac{\partial v_0}{\partial C_{\text{Prec}}} \cdot f_\alpha + v_0 \cdot \frac{\partial f_\alpha}{\partial C_{\text{Prec}}} \cdot \exp\left(\frac{-E_i}{RT}\right) \]

\[ \frac{\partial K_i}{\partial C_{SS}} = K_{i0} \cdot (\frac{\partial v_0}{\partial T} \cdot f_\alpha \cdot \exp\left(\frac{-E_i}{RT}\right) \]

Volume fraction of \( \alpha \) phase:

\[ f_\alpha = 1 - \frac{x_P}{x_\delta - x_\alpha} \]

\[ \frac{\partial f_\alpha}{\partial T} = \frac{x_P}{(x_\delta - x_\alpha)^2} \left( \frac{\partial x_\delta}{\partial T} + \frac{\partial x_\alpha}{\partial T} \right) \]

\[ \frac{\partial f_\alpha}{\partial C_{\text{Prec}}} = -1 \times \frac{\partial x_P}{x_\delta - x_\alpha \cdot \partial C_{\text{Prec}}} \]

Atomic fraction of hydride:

\[ x_P = \frac{C_{\text{Prec}}}{C_{\text{Prec}} \cdot (1 - \frac{M_H}{M_{Zr}}) + 10^6 \cdot \frac{M_H}{M_{Zr}}} \]

\[ \frac{\partial x_P}{\partial C_{\text{Prec}}} = \frac{1}{C_{\text{Prec}} \cdot (1 - \frac{M_H}{M_{Zr}}) + 10^6 \cdot \frac{M_H}{M_{Zr}}} + C_{\text{Prec}} \cdot (C_{\text{Prec}} \cdot (1 - \frac{M_H}{M_{Zr}}) + 10^6 \cdot \frac{M_H}{M_{Zr}})^2 \]

Atomic fraction of hydrogen at the \( \alpha/\alpha + \delta \) boundary:

\[ x_\delta(T) = -9.93 \times 10^{-11} \cdot T^3 + 8.48 \times 10^{-8} \cdot T^2 - 5.73 \times 10^{-5} \cdot T + 0.623 \]

\[ \frac{\partial x_\delta}{\partial T} = -3 \times 9.93 \times 10^{-11} \cdot T^2 + 2 \times 8.48 \times 10^{-8} \cdot T - 5.73 \times 10^{-5} \]
Atomic fraction of hydrogen:

\[
v_0 = \frac{x_0 - x_\alpha}{x_\delta - x_\alpha}
\]

\[
\frac{\partial v_0}{\partial T} = -\frac{\partial x_\alpha}{\partial T} \frac{1}{x_\delta - x_\alpha} - \frac{x_0 - x_\alpha}{(x_\delta - x_\alpha)^2}
\]

\[
\frac{\partial v_0}{\partial C_{Prec}} = \frac{\partial v_0}{\partial C_{SS}} = \frac{\partial x_0}{\partial C_{Prec}} \frac{1}{x_\delta - x_\alpha}
\]

Atomic fraction of hydrogen:

\[
x_0 = \frac{C_{tot}}{C_{tot} \cdot (1 - \frac{M_H}{M_Zr}) + 10^6 \cdot \frac{M_H}{M_Zr})}
\]

\[
\frac{\partial x_0}{\partial C_{Prec}} = \frac{\partial x_0}{\partial C_{SS}} = \frac{1}{C_{tot} \cdot (1 - \frac{M_H}{M_Zr}) + 10^6 \cdot \frac{M_H}{M_Zr})} + C_{tot} \cdot (1 - \frac{M_H}{M_Zr}) + 10^6 \cdot \frac{M_H}{M_Zr}))^2
\]

Atomic fraction of hydrogen in the \( \alpha \) phase:

\[
x_\alpha = \frac{TSS_D}{TSS_D \cdot (1 - \frac{M_H}{M_Zr}) + 10^6 \cdot \frac{M_H}{M_Zr})}
\]

\[
\frac{\partial x_\alpha}{\partial C_{Prec}} = \frac{TSS_D}{TSS_D \cdot (1 - \frac{M_H}{M_Zr}) + 10^6 \cdot \frac{M_H}{M_Zr})} + TSS_D \cdot (1 - \frac{M_H}{M_Zr}) + 10^6 \cdot \frac{M_H}{M_Zr}))^2
\]
Bibliography


