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COUPLED BISON/THERMOCHIMICA SIMULATION OF HYDRIDE FORMATION IN ZIRCALLOY CLADDING

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ABSTRACT

The report describes implementation of the thermodynamics models for simulation of zirconium hydride formation in LWR fuel cladding. The current models for ZrH$_x$ formation are based on empirical rate models that must calibrated to materials and regimes of interest. The thermodynamic approach enables hydride formation calculations based on fundamental thermodynamics principles and material composition. Thermodynamic formulations and models were implemented in the Idaho National Laboratory fuel performance code Bison using Material, Kernel and AuxKernel methods. The results for the Material and Kernel implementation are shown in this report. The Material method implementation naturally fits the concept of modeling evolution of material state in the material models. Given the relatively high cost of thermodynamic computation, the advantage of the AuxKernel compared to Material implementation is the ability to control the execution and computational cost. The implemented formulations are illustrated on example problems which fit the experimental data and satisfy the computational requirements of conservation equations.

1. INTRODUCTION

Hydrogen absorption and formation of hydrides in the cladding tubes of nuclear fuel elements can be detrimental their structural integrity [1]. Depending on the operating conditions, the absorbed hydrogen can exist in a solid solution of zirconium alloy, or it can bond with zirconium into various hydride forms. The associated misfit strains between metal and hydride phases lead to elastic and plastic deformations, internal stresses and stress concentrations [2, 3]. The understanding and prediction of formation, distribution, and morphology of hydrides are important for extending the burnup of nuclear elements [4].

The hydrogen ingress into fuel element cladding can be related to the fuel burnup and corrosion [1]. Once the solubility of the hydrogen in Zircaloy metal matrix has been exceeded, various forms of hydrides begin to form. The hydride precipitation and dissolution models are based on super- and under- saturation of hydrogen, respectively, from the normal solution state in the metal matrix. The experiments have shown hysteresis in the process of precipitation and dissolution, that are described by two equilibrium parameters, Terminal Solid Solubility for precipitation (TSSp), and Terminal Solid Solubility for dissolution (TSSd) [5, 6]. The departure from the equilibrium conditions is used as the driving force for the kinetics of the process [7-9]. These models for zirconium hydride kinetics [10, 11] have been recently implemented in the INL nuclear fuel performance code Bison [12]. The models depend on calibration of various equilibrium and kinetic parameters. It was argued that the composition has little effect on the solubility parameters [5, 7, 13], although the authors provide notably different values.

In contrast to the kinetic models, the thermodynamic models determine the equilibrium chemical composition of the material. They do not consider the kinetics of the chemical process. For a given elemental composition, pressure and temperature, the equilibrium solver determines a unique combination of phases and their compositions at thermochemical equilibrium. Chemical equilibrium is not achieved instantaneously, but the chemical kinetics may not be very significant for sufficiently high temperatures, long time periods, and when atoms of the various chemical elements are randomly mixed in the system. In nuclear fuels problems under normal operating conditions, chemical equilibrium is achieved quickly due to the high temperatures, and the chemical reactions occur over long time periods. Thermochimica
[14] is a software library developed for calculation of thermochemical equilibrium at a prescribed composition, temperature and pressure. It has been integrated into nuclear fuel code Bison and used for modeling various aspects of nuclear chemistry. Thermochemica model consists of a library of material thermodynamic properties, thermodynamic models, and a numerical solver to minimize global Gibbs energy while respecting the Gibbs Phase Rule and conservation of mass.

In this report, we describe the implementation of the thermodynamic-based model for the Zr-H system for modeling zirconium hydride formation in nuclear fuel element cladding. The Zr-H material system is described by a thermodynamic model which is used as an input for the thermodynamic equilibrium solver. In the next section, we provide a brief description of the thermodynamic model for Zr-H system. The implementation of various Zircaloy models is available in the literature which can be substituted into the existing framework. The implementation of the model in Bison using Material, Kernel and AuxKernel modules is described after that. Finally, simple benchmark examples are presented illustrating the performance and consistency of the implementation. A journal paper is in preparation. It will compare the models with experiments for which additional Zircaloy thermodynamic material models are under development.

2. THERMODYNAMIC MODELS FOR ZIRCONIUM – HYDROGEN SYSTEM

The thermo-chemical solver, Thermochimica, was used for determining equilibrium phases for the Zr-H system, their chemical composition and distribution, including metallic Zr phases with dissolved H. The results from the thermo-chemical solver can also be used for determining other physical properties and models, such as heat capacity, thermal conductivity, etc.

Figure 1 shows the phase diagram of the Zr-H system created using the developed thermodynamic model based on reference [15]. The phase diagram illustrates the primary phase regions of interest on the lower hydrogen side of the diagram: hexagonal closed packed (hcp) $\alpha$-Zr, body centered cubic (bcc) $\beta$-Zr, face centered cubic (fcc) $\delta$-ZrH$_{2-x}$, and the two-phase regions $\alpha+\beta$ and $\alpha+\delta$. 

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Figure 1. Zirconium-Hydrogen Phase Diagram as Calculated by Thermochimica

Thermochimica calculations were in a close agreement with the commercial thermochemical equilibrium solver FactSage [16]. The α-Zr solid solution has a maximum hydrogen solubility of 5.5 at.% at ~615°C. However, at the nominal outer clad wall temperature of 340°C and inner wall temperature of 375°C, the terminal hydrogen solubility is ~0.83 at.% and ~1.1 at.%, respectively. In this temperature range, the δ phase will begin to precipitate once the solubility limit has been reached.

3. IMPLEMENTATION OF ZIRCONIUM HYDRIDING MODEL INTO FEM CODE BISON

The developed material and transport models use two variables for describing hydrogen in the system. Concentrations are expressed in terms of the amount of hydrogen in a specific phase with respect to the total volume of a computational element (i.e. finite element) that contains all phases. The first variable, named Css, represents wt.ppm concentration of hydrogen in the α phase (metallic Zr containing dissolved H, where H occupies tetrahedral sites within the hcp cell). The second variable, Cp, represents wt.ppm concentration of hydrogen in the hydride phases, in our case δ phase (ZrH_{2-x}), that is assumed to be immobile and not participating in hydrogen diffusion. In contrast to models that use separate rate equations for hydrogen transitioning between the two phases, we use the thermodynamics solver to partition the two phases and their respective species. It is assumed that hydrogen in Css is diffusing and thus it is used as the basic variable for the hydrogen diffusion model. The diffusion volume does not change during simulation as it is assumed that the volume fraction of the δ phase is small.
The model includes several coupled physics models:

a) heat equation

\[ \rho C_p \frac{\partial T}{\partial t} - \nabla \cdot k \nabla T - \dot{q} = 0 \]

b) hydrogen transport

\[ J = -D \left( \nabla H_{ss} + \frac{Q^* H_{ss}}{RT^2} \nabla T \right) - \frac{\partial H_{ss}}{\partial t} - \nabla \cdot J - Q = 0 \]

c) zirconium hydride precipitation and dissolution

\[ Q = \frac{H_{ZrH_s}^{(t+\Delta t)} - H_{ZrH_s}^{(t)}}{\Delta t} \]

where \( H_{ss} \) denotes volume concentration of hydrogen that is contained solid solution, i.e. value derived from \( C_{ss} \). \( H_{ZrH_s} \) denotes concentration of hydrogen stored in hydrides, i.e. valued derived from \( C_p \). The rest of the symbols conform to the standard nomenclature of the respective equations.

The thermodynamic model for the Zr-H material system is implemented using Bison Material method. The source/sink is implemented using the Kernel method. The alternative implementation uses the AuxKernel method. The AuxKernel implementation has advantage that user can control the evaluation and, thereby, manage the computational cost, which for thermodynamic solvers is considerable. In this report, only the Material method implementation will be used as the AuxKernel implementation may have to be adjusted due to recent changes in Bison.

The Material model is implemented in updated version of MaterialHZrH.C function. The updated hydrogen source/sink Kernel is HZrHSourse.C. The latter is used for both \( C_{ss} \) and \( C_p \) variables, but with different signs since the source of one is the sink of the other, and vice versa. Monomial, constant value finite elements are more practical in cases where large variations of the values occur.

4. SIMULATION EXAMPLES

Several example cases were used to validate the model. The tested thermodynamic model for Zr-H system has a lower solubility limit compared to values used in literature. Models for Zircalloys are under implementation and compared to the experimental data. The first set of experiments used one fine element with prescribed temperature and hydrogen concentration. The partition of the hydrogen into solid solution and hydrides for different temperatures (T) and initial hydrogen concentrations (H) is shown in Figure 2.
Figure 2: Concentration of hydrogen in hydrides (Cp) and solid solution (Css) for different temperatures (T) and initial hydrogen concentration (H).

The partition of hydrogen agrees with the thermodynamic model and phase diagram. The constant value and conservation over the simulation time illustrate the stability of the model.

The next example uses one variable, hydrogen in solid solution, Css, and monomial finite elements. The initial concentration of 400 wt.ppm of hydrogen is used. Temperature gradient of 100 K is imposed. The evolution of hydrogen concentration in solid solution and hydrides, temperatures, and total hydrogen is shown in Figure 3. The total concentration stays constant which shows the stability of the implemented methods.
Figure 3: Evolution of hydrogen concentration in hydrides (top bar), hydrogen concentration in solution (second bar from the top), temperature (third bar), and total hydrogen concentration (fourth bar).

In the next example, we use linear finite elements. In this case we use two variables similar to the implementation in References [10, 11]. The first variable represents the hydrogen in solid solution, $C_{ss}$, and the second variable, $C_{p}$, represents the hydrogen in hydrides.
As for the case of the monomial finite elements, the total concentration of hydrogen is conserved, and the values correspond to the equilibrium values for the thermodynamic model.

Figure 4: Evolution of hydrogen concentration in hydrides (top bar), hydrogen concentration is solution (second bar from the top), and temperature (third bar)
5. SUMMARY

We have developed thermodynamics-based model for precipitation, dissolution and transport of hydrogen in zirconium hydrogen system. The model used two variables for describing partition of hydrogen concentration in the system, (a) hydrogen in the α zirconium phase and (b) hydrogen in the ZrH_{2-x}δ phase. Partitioning of hydrogen between the two phases is based on thermochemical equilibrium model for the system. The model is implemented in finite element method code Bison using Material, Kernel, and AuxKernel methods. The implementation is demonstrated on simple examples with constant and varying temperatures.

6. ACKNOWLEDGEMENTS

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7. REFERENCES


