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A quantitative phase field model for hydride precipitation in zirconium alloys: Part I. Development of quantitative free energy functional

San-Qiang Shi[1]* and Zhihua Xiao

The Hong Kong Polytechnic University Shenzhen Research Institute, Shenzhen 518057, China

Department of Mechanical Engineering, Hong Kong Polytechnic University

Hung Hom, Kowloon, Hong Kong, China

Abstract

A temperature dependent, quantitative free energy functional was developed for the modeling of hydride precipitation in zirconium alloys within phase field scheme. The model takes into account of crystallographic variants of hydrides, interfacial energy between hydride and matrix, interfacial energy between hydrides, elastoplastic hydride precipitation and interaction with externally applied stress. The model is fully quantitative in real time and real length scale, and simulation results were compared with limited experimental data available in the literature with a reasonable agreement. The work calls for experimental and/or theoretical investigations of some of the key material properties that are not yet available in the literature.

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*Corresponding author. E-mail: mmsqshi@polyu.edu.hk.
Tel.: +852 27667821. Fax: +852 23654703.

1. Introduction

Zirconium alloys are used in nuclear power plants due to good mechanical properties, corrosion resistance and low neutron adsorption cross-section. During the service, these alloys pick up hydrogen from the working environment and when the hydrogen solid solubility limit is reached, brittle hydrides will form, which can reduce the fracture toughness of the alloys by orders of magnitude. There have been extensive studies on zirconium hydrides both experimentally and theoretically, see for example, a recent comprehensive review by Puls [1]. There are different types of hydrides such as ζ (Zr_2H), γ (ZrH), δ ($ZrH_{1.6}$, most popular in reactor condition) and ε (ZrH_2). Hydride growth involves plastic deformation around hydrides in the metal lattice. There is a significant hysteresis in hydrogen solid solubility in zirconium, depending on the thermal and mechanical history of the component. External stress may affect the orientation of hydrides. Hydride morphology (such as orientation, density and distribution, especially around cracks) will strongly affect the fracture behavior of the alloys. Due to the complexity of the problem, early theoretical studies had made simplified assumptions on hydride morphology [2-5], which is not realistic as compared to experimental observations. In recent years, attempts were made to model hydride morphology using phase field methods (PFM) [6-12]. PFM describes microstructures of a system using a set of conserved and nonconserved field variables that are continuous across the interfacial regions. The temporal and spatial evolution of the field variables is governed by the Cahn-Hilliard nonlinear diffusion equation and the Allen-Cahn relaxation equation. With the fundamental thermodynamic and kinetic information as the input, the phase-field method is able to predict the evolution of arbitrary morphologies and complex microstructures without explicitly tracking the positions of interfaces [13]. Using PFM, we had studied the effect of stress [6,7], grain boundary [8], and defects such as cracks [9], on the hydride morphology evolution.

We used a set of order parameters to describe different crystallographic variants of hydrides and also included the effect of plastic deformation in simulations. Thuinet et al. [11,12] considered only the elastic deformation and were able to predict hydride morphology with threefold symmetry with only one order parameter. All PFM models developed so far are not fully quantitative: although the effects of stress and strain are quantitatively described, the time and space are not in real scale and temperature effect is not fully included. It is very important to develop a fully quantitative PFM in order to study the effects of temperature transient and temperature gradient.

For a fully quantitative modeling of microstructure evolution in materials by phase field method, the most important task is to construct the free energy functional (F) of the system. A general form of F for a binary alloy system is

$$F = \int \left[f(C, \eta_p) + \sum_p \frac{\kappa_p}{2} \left(\nabla \eta_p \right)^2 + \frac{\lambda}{2} \left(\nabla C \right)^2 + E_{strain} + W \right] dV \tag{1}$$

where $f(C, \eta_p)$ is the chemical free energy density (also called the bulk free energy density) which can be a function of the composition C (conserved variable) and long-range order parameters η_p (non-conserved variables), followed by two gradient terms related to interfacial energy (κ_p and λ are gradient coefficients. The interfaces are assumed isotropic and coherent), strain energy (E_{strain}) and the work done (W) by other forces such as electrical or magnetic forces. The volumetric integration is conducted over the entire system. The latter two energy terms have been quantitatively examined elsewhere (see for example, references [14,15] for studies on strain energy). This study focuses on quantifying the chemical and gradient terms.

We consider Zr-H systems that undergo phase transformation according to the phase diagram, Figure 1. The hydrogen composition variable C refers to mole fraction or atomic fraction of hydrogen in zirconium. The composition C_0 is the starting composition (average composition) of hydrogen. C_α and C_β refer to the composition in the disordered (in solid solution) and ordered phases (in hydrides) at thermodynamic equilibrium, respectively. Both C_α and C_β may be functions of temperature. C_α is also commonly considered the solid solubility limit of hydrogen in zirconium. The ordered phase may have several energetically identical but crystallographically different variants. In this case, a set of long-range order parameters (η_p, where p=1, 2, 3…) is needed to describe the ordered phases.

A Landau polynomial is often used for the chemical free energy density (f). An expression of the chemical free energy density has been proposed [6,16,17] as follows.

$$f(C,\eta_p) = A_0 + \frac{A_1}{2}(C-C_1)^2 + \frac{A_2}{2}(C_2-C)\sum_p \eta_p^2 - \frac{A_3}{4}\sum_p \eta_p^4 + \frac{A_4}{6}\sum_p \eta_p^6 + A_5\sum_{p\neq q}\eta_p^2\eta_q^2 + A_6\sum_{p\neq q,q\neq r}\eta_p^4(\eta_q^2+\eta_r^2) + A_7\sum_{p\neq q\neq r}\eta_p^2\eta_q^2\eta_r^2 \tag{2}$$

In this expression, the phenomenological parameters A_1~A_7 should be positive values. Although A_0 should come from the thermodynamic data of the alloy, its value will not affect the accuracy of the microstructure evolution prediction and is thus ignored in the following discussion. The four terms (A_1~A_4) provide local minima of f at $C=C_1$, $\eta_p=0$ (the disordered phase), and at $C=C_2$, $\eta_p=\eta_{eq}$, where η_{eq} is the equilibrium value of η_p in the ordered phases. The last three terms (A_5~A_7) ensure that, (1). it is energetically expensive to produce two or more different ordered variants at the same location; and (2). these parameters affect the transition path during order-disorder transformation in the free energy surface. Later we will show that these three parameters are related to the interfacial energy and interfacial thickness between different variants of the β

phase. A schematic plot of f as a function of composition is given in Figure 2. Note the different definitions of C_1, C_2, C_α, and C_β: the chemical free energy density (f) reaches the local minima at C_1 (if η=0) and C_2 (if η_p=±1), whereas C_α and C_β provide the equilibrium composition when the disordered and ordered phases reach the state of thermodynamic equilibrium.

It should be noted that most parts of the chemical free energy density expression (f) are in fact non-equilibrium free energies. Therefore the mathematic description of this density is not unique, even for the same material system. There were some efforts in the literature trying to quantify the chemical free energy density, such as [18-20]. However, most of them have often chosen the phenomenological parameters for the convenience of numerical simulation. As a result, phase field simulations can only provide qualitative or semi-quantitative predictions of microstructure evolution. In this work, we aim to develop a physically sound Landau polynomial and gradient coefficients that are a function of temperature and can be used to quantitatively predict the phase transformation and associated microstructure evolution in real time and real length scale. As is shown later, this task requires the accurate treatment of the free energies near compositions C_1, C_2, C_α, and C_β, and a detailed knowledge of the thermodynamic driving force of the phase transformation.

2. Phenomenological Parameters A_1~A_4 in f

Without loss of generality, take only one variant η_p as an example (i.e., let $\eta_p=\eta$) and consider only the terms A_1~A_4 first. We assume that the driving force of the phase transformation is given by $\Delta g=A_1/2$ and is independent of the internal state variable η. We determine the value of Δg later. The chemical free energy density is simplified to

$$f(C,\eta) = \Delta g(C - C_1)^2 + \frac{A_2}{2}(C_2 - C)\eta^2 - \frac{A_3}{4}\eta^4 + \frac{A_4}{6}\eta^6 \tag{3}$$

From (3), the first partial derivative of f to η results in

$$\frac{\partial f}{\partial \eta} = A_2(C_2 - C)\eta - A_3\eta^3 + A_4\eta^5 \tag{4}$$

If C=C_2, the first term in (4) vanishes, and (4)=0 because it is in the ordered phase (at a minimum of f). We find that

$$\eta^3(-A_3 + A_4\eta^2) = 0 \qquad \text{(when } C\text{=}C_2\text{)} \tag{5}$$

This equation has three solutions: η=0 (f reaches a local maximum, an unstable state), and $\eta^2 = \frac{A_3}{A_4}$ (f reaches local minima at equilibrium state). Thus,

$$\eta_{eq} = \pm\sqrt{\frac{A_3}{A_4}} \tag{6}$$

For the sake of convenience, let A_3=A_4 in the following work so that η_{eq}=±1. The values of +1 and -1 may represent an ordered phase and its anti-phase, respectively (Two ordered phases share the same crystalline orientation with mirror-image symmetry. This is true for γ-hydrides). Otherwise, both values of η_{eq} can be treated as the same variant phase.

Further, from (3), the first partial derivative of f to C results in

$$\frac{\partial f}{\partial C} = 2\Delta g(C - C_1) - \frac{A_2}{2}\eta^2 \tag{7}$$

At η=±1 (in the ordered phase), C=C_2. Let (7)=0 (required by the local minimum), we have

$$A_2 = 4\Delta g(C_2 - C_1) \tag{8}$$

Inspecting (3), we see that when $C=C_1$ and $\eta=0$, $f(C_1, 0)=0$, f reaches its first minimum in the disordered phase. However, when $C=C_2$ and $\eta=\pm1$, f reaches the other two minima at $f(C_2, \pm1)$ in the ordered phase:

$$f(C_2,\pm1) = \Delta g(C_2 - C_1)^2 - \frac{A_3}{4} + \frac{A_3}{6} \tag{9}$$

Note that we used the condition $A_3=A_4$ in (9). From (9), we find that

$$A_3 = A_4 = 12[\Delta g(C_2 - C_1)^2 - f(C_2,\pm1)] \tag{10}$$

In general, $f(C_2, \pm1)\neq0$, even when $f(C_1, 0)$ is set to 0. The value of $f(C_2, \pm1)$ should come from the thermodynamic data of a specific alloy. However, in phase field modeling it is often adequate to define the relative magnitude of the minima $f(C_2, \pm1)$ with reference to the magnitude of f at the first minimum, $f(C_1, 0)$. The determination of $f(C_2, \pm1)$ can be based on the fact that the disordered and order phases share the same value of chemical potential at the equilibrium state - a common tangent line (y) at the two compositions C_α and C_β near the two minima $f(C_1, 0)$ and $f(C_2, 1)$ in the f-C-η space (see Figure 2). This consideration results in

$$f(C_\beta,\pm1) = (C_\beta - C_\alpha)\frac{\mu_\alpha}{V_\alpha} + f(C_\alpha,0) = (C_\beta - C_\alpha)\frac{\mu_\alpha}{V_d} \tag{11}$$

where μ_α and V_α are the chemical potential and mole volume of the disordered phase, respectively. A solution model for the Zr-H system is required to determine the chemical potential μ_α. For a regular solution [21],

$$\mu_\alpha = \omega(1 - C_\alpha)^2 + RT\ln C_\alpha \tag{12}$$

where R is the gas constant, T is the absolute temperature, and ω is the formation energy of hydrogen interstitials in solid solution, which may be estimated by [21]

$$\omega = \frac{RT}{2C_1 - 1} \ln \frac{C_1}{1 - C_1} \tag{13}$$

Putting (12) and (13) into (11) and ignoring the small difference between $f(C_2, \pm 1)$ and $f(C_\beta, \pm 1)$,

$$f(C_2, \pm 1) \approx f(C_\beta, \pm 1) = (C_\beta - C_\alpha) \frac{RT}{V_\alpha} \left[\frac{(1 - C_\alpha)^2}{2C_1 - 1} \ln \frac{C_1}{1 - C_1} + \ln C_\alpha \right] \tag{14}$$

When C_1 and C_α are both small, (14) simplifies to

$$f(C_2, \pm 1) \approx (C_\beta - C_\alpha) \frac{RT}{V_\alpha} \ln \frac{C_\alpha}{C_1} \tag{15}$$

It is clear from (15) that if $C_1 > C_\alpha$, then $f(C_2, \pm 1) < 0$, resulting in a negative slope of the common tangent line y; otherwise the slope is positive. Using (15), (10) changes to

$$A_3 = A_4 \approx 12[\Delta g (C_2 - C_1)^2 - (C_\beta - C_\alpha) \frac{RT}{V_\alpha} \ln \frac{C_\alpha}{C_1}] \tag{16}$$

We find $A_1 \sim A_4$ to be functions of the driving force Δg in (8) and (16). In the following section, we will discuss how to evaluate Δg, the gradient coefficients (κ, λ), and C_1.

3. Δg, Gradient Coefficients and C_1

Let's consider the interface between a hydride and zirconium metal phase. In this situation, the contribution of $A_5 \sim A_7$ to the local free energy vanishes. We also assume that the interfaces between hydride and metal matrix are coherent, and that the interfacial properties are isotropic and independent of the ordered variants. In fact, this is not exactly true because it has been observed that dislocation loops can be generated from the interface when hydride size is large enough, which result in incoherent interfaces. However, the energy related to incoherency may be accounted for by introducing plastic deformation into the phase field model, as we have done before [7,9]. Therefore the above assumption can greatly simplify the formulation. Then (1) changes to

$$F = \int \left[f(C,\eta_p) + \frac{\kappa}{2}\sum_p \left(\nabla \eta_p\right)^2 + \frac{\lambda}{2}(\nabla C)^2 + E_{strain} + W \right] dV \tag{17}$$

In a one-dimensional analysis in which only one flat interface is present and when the strain energy and work terms are absent, the interfacial energy (γ_S) between the hydride and metal matrix phases is [21],

$$\gamma_s = 2\int_{C_\alpha}^{C_\beta} \left(\frac{\lambda}{2} \Delta f(C,\eta) \right)^{1/2} \left[1 + \frac{\kappa}{\lambda}\frac{d\eta}{dC} \right]^{1/2} dC \tag{18}$$

where C and η are the equilibrium distributions across the interface region, and κ and λ are constants for a given temperature. For simplicity, it is assumed that $\frac{\kappa}{\lambda}\frac{d\eta}{dC} = 1$, unless a better knowledge of κ and λ is available so that

$$\gamma_s = 2\int_{C_\alpha}^{C_\beta} \left[\lambda \cdot \Delta f(C,\eta)\right]^{1/2} dC = 2\int_{C_\alpha}^{C_\beta} \left[\lambda \cdot \{ f(C,\eta) - y(C,\eta) \}\right]^{1/2} dC \tag{19}$$

where $y(C, \eta)$ is the common tangent line between the minima $f(C_\alpha, 0)$ and $f(C_\beta, \pm 1)$. Following the same reasoning as in (11) and considering the f-η plane, a linear relationship such as $\frac{y(C,\eta) - f(C_\alpha,0)}{\eta - 0} = \frac{f(C_\beta,1) - f(C_\alpha,0)}{1-0} = (C_\beta - C_\alpha)\frac{\mu_\alpha}{V_\alpha}$ is apparent. This relationship provides the y function as

$$y(C,\eta) = (C_\beta - C_\alpha)\frac{\mu_\alpha}{V_\alpha}\eta \tag{20}$$

In (20), η is linearly related to C along the straight line between the two minima (see Figure 3(b)), that is,

$$\eta = \frac{C - C_\alpha}{C_\beta - C_\alpha} \tag{21}$$

This linearity, together with the assumption of $\frac{\kappa}{\lambda}\frac{d\eta}{dC} = 1$, results in

$$\kappa = \lambda(C_\beta - C_\alpha) \tag{22}$$

Putting (3), (20) and (21) into (19) and using the constants ($A_1 \sim A_4$) developed in an earlier section, we arrive at

$$\gamma_s = 2[\lambda\Delta g]^{1/2}(C_\beta - C_\alpha)^2 I \tag{23}$$

where

$$I = \int_0^1 \left\{ 3\eta^2 - 2\eta^3 - 12\left[\frac{1}{4} - \frac{1}{6}\eta^2\right]\eta^4[1-a] - a\eta \right\}^{1/2} d\eta \tag{24}$$

and

$$a = \frac{RT}{V_\alpha \cdot \Delta g \cdot (C_\beta - C_\alpha)}\left[\frac{(1-C_\alpha)^2}{2C_1 - 1}\ln\frac{C_1}{1-C_1} + \ln C_\alpha\right] \tag{25}$$

Or,

$$\Delta g = \frac{RT}{V_\alpha \cdot a \cdot (C_\beta - C_\alpha)}\left[\frac{(1-C_\alpha)^2}{2C_1 - 1}\ln\frac{C_1}{1-C_1} + \ln C_\alpha\right] \tag{26}$$

If both C_α and C_1 are much smaller than unity (this is the case for Zr-H system at reactor condition),

$$\Delta g \approx \frac{RT}{V_\alpha \cdot a \cdot (C_\beta - C_\alpha)}\ln\frac{C_\alpha}{C_1} \tag{27}$$

We then rearrange (23) as

$$\lambda = \frac{\gamma_s^2}{4(C_\beta - C_\alpha)^4 I^2 \Delta g} \tag{28}$$

From (22) and (28), one can see that if a, Δg and γ_s are known, the values of gradient coefficients (κ and λ) can be obtained. Since Δg is determined by the parameters a and C_1 through equations (26) or (27), we need to define a and C_1 first. For a, we consider the interface thickness between hydride and metal matrix (l). Assume that $\Delta f(C, \eta)$ reaches the maximum ($\Delta f_{\max}$) at $C \approx (C_1+C_2)/2$ and $\eta \approx 1/2$:

$$\begin{aligned}\Delta f_{\max} &\approx f(\frac{C_1+C_2}{2},\frac{1}{2}) - y(\frac{C_1+C_2}{2},\frac{1}{2}) \\ &= \frac{\Delta g}{2}(C_2-C_1)^2\left[1-\frac{5}{16}(1-a)-a\right]\end{aligned} \tag{29}$$

The interfacial thickness (l) can then be estimated by [21]

$$l = (C_\beta - C_\alpha)\sqrt{\frac{\lambda}{2\Delta f_{\max}}} = \frac{\gamma_s}{2(C_\beta - C_\alpha)^2 \Delta g \cdot I\sqrt{1-\frac{5}{16}(1-a)-a}} \tag{30}$$

Here, an approximation of $C_2 - C_1 \approx C_\beta - C_\alpha$ is used. Since I and Δg are functions of a, (30) can be used to numerically determine the value of a under a given experimental condition, as long as C_1, γ_s and l are known. In general, C_1 may be obtained by thermodynamic calculation, and γ_s and l by first principles calculations or by experiments. For Zr-H system, there is no literature data on these three parameters (at least we did not find).

In order to use the above scheme for hydride modeling, we estimate C_1 as follows. Combining (27) and (30), one can find

$$C_1 = C_\alpha \exp\left[-\frac{\gamma_s}{l}\cdot\frac{V_\alpha}{RT}\cdot\frac{a}{2(C_\beta - C_\alpha)I\sqrt{1-\frac{5}{16}(1-a)-a}}\right] \tag{31}$$

When -2.5 < a < -1.8, $\frac{a}{I\sqrt{1-\frac{5}{16}(1-a)-a}} \approx -2.0$. Therefore,

$$C_1 \approx C_\alpha \exp\left[\frac{\gamma_s}{l}\cdot\frac{V_\alpha}{RT\left(C_\beta - C_\alpha\right)}\right] \tag{32}$$

Similarly, we may define C_2

$$C_2 \approx C_\beta \exp\left[\frac{\gamma_s}{l}\cdot\frac{V_\alpha}{RT\left(C_\beta - C_\alpha\right)}\right] \tag{33}$$

It should be emphasized that both (32) and (33) are assumptions for Zr-H system. Ideally, C_1 and C_2 should be determined by thermodynamic calculations. Put (32) in (27), we have

$$\Delta g \approx \frac{RT}{V_\alpha \cdot a \cdot (C_\beta - C_\alpha)} \ln\frac{C_\alpha}{C_1} = -\frac{\gamma_s}{l}\cdot\frac{1}{a\left(C_\beta - C_\alpha\right)^2} \tag{34}$$

The parameter a is a weak function of temperature at the reactor operating condition, as can be seen in Table 2.

4. Phenomenological Parameters A_5~A_7 in f

In order to estimate A_5~A_7, we further simplify our discussion by assuming that A_5=A_6=A_7. Here we ignore all possible variations in interfacial energy between two or three hydrides that are in contact. Consider only two hydrides (p and q) being in contact. At this interface, we assume that the concentration (C_2 or C_β) does not change across the interface, while the order parameter (η) changes from η_p to η_q, see Figure 4. Note from Figure 4 that the interface thickness is still assumed to be the same l defined in (30).

Then the chemical free energy density in the interface region becomes

(i) inside the hydride p ($0 \le$ x $\le l/2$):

$$f(C_2,\eta_p) = \frac{A_1}{2}(C_2 - C_1)^2 - \frac{A_3}{4}\left[1+\eta_q^4\right] + \frac{A_3}{6}\left[1+\eta_q^6\right] + A_5\left[\eta_q^2 + \eta_q^2\right] \tag{35}$$

where $|\eta_p| = 1$, and $\eta_q = \dfrac{2x}{l}$ (36)

(ii) inside the hydride q ($l/2 \le$ x $\le l$):

$$f(C_2,\eta_q) = \frac{A_1}{2}(C_2 - C_1)^2 - \frac{A_3}{4}\left[1+\eta_p^4\right] + \frac{A_3}{6}\left[1+\eta_p^6\right] + A_5\left[\eta_p^2 + \eta_p^2\right] \tag{37}$$

where $|\eta_q| = 1$, and $\eta_p = \dfrac{2l - 2x}{l}$ (38)

Away from the interface region and also inside the hydrides (x ≤ 0, or x $\ge 2l$), the chemical free energy density is

$$f(C_2,\eta) = \frac{A_1}{2}(C_2 - C_1)^2 - \frac{A_3}{4} + \frac{A_3}{6} \tag{39}$$

The interfacial energy (γ_h) between the two hydrides in one dimension is defined by

$$\begin{aligned}\gamma_h &= \int_{-\infty}^{+\infty}\left[\Delta f(C_2,\eta) + \frac{\kappa}{2}\sum_p(\nabla\eta_p)^2 + \frac{\lambda}{2}(\nabla C)^2\right]dx = \int_0^l\left[\Delta f(C_2,\eta) + \frac{\kappa}{2}\sum_p(\nabla\eta_p)^2\right]dx \\ &= \int_0^l\left[\Delta f(C_2,\eta)\right]dx + \int_0^l\left[\frac{\kappa}{2}\sum_p(\nabla\eta_p)^2\right]dx = I_1 + I_2\end{aligned} \tag{40}$$

Here, the condition $\nabla C = 0$ across the interface is applied, see Figure 4. The increase of chemical free energy density ($\Delta f(C_2,\eta)$) due to the existence of the interface can be estimated using (35) and (37) with reference to the average value of (39), such that

$$\begin{aligned}I_1 &= \int_0^l\left[\Delta f(C_2,\eta)\right]dx \\ &= \int_0^{l/2}\left[-\frac{A_3}{4}\eta_q^4 + \frac{A_3}{6}\eta_q^6 + 2A_5\eta_q^2\right]dx + \int_{l/2}^{l}\left[-\frac{A_3}{4}\eta_p^4 + \frac{A_3}{6}\eta_p^6 + 2A_5\eta_p^2\right]dx \\ &= l\left[\left(\frac{1}{42} - \frac{1}{20}\right)A_3 + \frac{2}{3}A_5\right] = l\left[-\frac{11}{420}A_3 + \frac{2}{3}A_5\right]\end{aligned} \tag{41}$$

$$I_2 = \int_0^l \left[\frac{\kappa}{2} \sum_p (\nabla \eta_p)^2 \right] dx = \int_0^{l/2} \left[\frac{\kappa}{2} \left(\frac{2}{l} \right)^2 \right] dx + \int_{l/2}^{l} \left[\frac{\kappa}{2} \left(\frac{-2}{l} \right)^2 \right] dx = \frac{2\kappa}{l} \tag{42}$$

In the above integrations, linear relations (36) and (38) are used. Combine (40), (41) and (42), and rearrange terms, we find

$$A_5 = \frac{3}{2} \left[\frac{\gamma_h}{l} + \frac{11}{420} A_3 - \frac{2\kappa}{l^2} \right] \tag{43}$$

At this point, all of the parameters in the free energy functional (17) are now in principle measurable or quantifiable. It should be pointed out that it is often necessary to introduce a modification factor to the strain energy (E_{strain}) and/or to the work done by external forces (W) in (17) in order to properly account for the effect of mechanical and/or other external forces during phase transformation. This factor can be determined through properly designed experimental tests under external forces. Thus, quantitative modeling of the microstructure evolution can be performed by numerically solving the following set of dynamic equations simultaneously

$$\frac{\partial C}{\partial t} = \nabla \cdot \left(M \nabla \frac{\delta F}{\delta C} \right) + \xi \tag{44}$$

$$\frac{\partial \eta_p}{\partial t} = -L_p \frac{\delta F}{\delta \eta_p} + \zeta_p \qquad (p=1, 2, 3\ldots) \tag{45}$$

M is the chemical mobility related to the diffusion of hydrogen in the alloy [19], while L_p is the mobility of the order parameters η_p at the interface between two phases (α and β). ξ and ζ_p are the terms to represent sinks, sources, or thermal fluctuation in the system. If the phase transformation is controlled by the diffusion process, one can set $L_p \geq M/(\Delta l)^2$ where Δl is the grid size in a numerical scheme, so that the slower process (i.e. chemical diffusion) will control the interface movement during phase transformation.

5. Verification of the Model

In order to verify the above model, one needs to compare the model predictions against experimental data. However, in addition to the lack of critical parameters in the literature such as interfacial energy (γ_s and γ_h), well-defined and quantitative experiments on hydride nucleation and growth in zirconium are very rare. For example, in many experiments, materials properties such as elastic modulus, yield strength, hydrogen diffusion coefficient and so on, were not measured, which are important for quantitative modeling. Bailey had conducted TEM studies on γ-hydride precipitation in zirconium [22]. One of Bailey's work was the TEM observation of fast quenched specimen from 800 ºC with about 4 at% of hydrogen. γ-hydrides are needle-shaped particles formed by fast cooling. The needle axis has three equivalent directions of the $\left[11\bar{2}0\right]$ type on the basal plane of the hexagonal zirconium single crystal. Bailey had observed micro meter sized needle shape hydrides with dislocation loops around them, indicating plastic deformation during hydride growth.

To simulate hydride formation under Bailey's experimental condition, we need to first quantify a using (28) and then Δg using (25). The material properties such as V_α, C_α (hydrogen solid solubility in zirconium), and C_β (hydrogen composition in hydride) were measured, see Table 1. Since the interfacial properties were never measured or theoretically estimated. Therefore, we assume $\gamma_s = 0.1$ J/m^2, $l = 0.5$ nm, and $A_5 = 0.08A_3$. We used (32) and (33) to define C_1 and C_2, respectively. C_α is defined by the terminal solid solubility of hydrogen for hydride precipitation in zirconium (TSSP). Slattery's result was converted to atomic percent and applied to C_α [23]. For γ-hydrides, $C_\beta = 0.50$. The mobility coefficient M for hydrogen in zirconium was estimated in terms of f and the hydrogen diffusion coefficient D by $M = \frac{D}{\partial^2 f / \partial C^2} = \frac{D}{2\Delta g}$. The strain energy term in (17) must include the effect of plastic deformation, especially during the hydride growth stage. This requires an additional set of phase field equations for plastic deformation. Detailed descriptions of the computational procedures were given elsewhere [7,9,15]. Applying the scheme developed in this work and using the material parameters listed in Table 1 (Bailey did not provide these materials properties [22]), we are able to predict the evolution of hydride precipitation morphology in real-time and real-length scales, see Figure 5. The prediction compares reasonably well to Bailey's observation in terms of both the hydride size and density.

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Table 1. Material parameters used in the modeling of γ-hydride precipitation in zirconium.

T=300 K

R=8.314 $J/mole\ K$

C_0=0.04, C_α= 3.75exp(-28000/RT), C_β=0.50

γ_s=0.10 J/m^2, l = 0.50nm, $\frac{\gamma_s}{l}$=2×10^8 J/m^3

V_α=1.67×10^{-6} m^2/s

D=4.1×10^{-7} exp(-38400/RT) m^2/s

$A_5 = 0.08A_3$

Yield stress is 782 MPa, Young's modulus 94.35 GPa, Poisson ratio 0.436. Plastic effect is applied at 0.15 second.

Modification factor on strain energy = 4.0

Eigen strains of hydrogen interstitials and γ-hydride as well as elastic and plastic constants of zirconium are given in reference [7].

Table 2. Parameter *a* calculated by (30)

T(K)	*a*
300	-2.139
350	-2.123
400	-2.093
450	-2.052
500	-2.015
550	-2.003
600	-2.037
650	-2.141
700	-2.347
750	-2.698
800	-3.270
850	-4.207
900	-5.811

The following figures are not included in the above manuscript, but it may be a good idea to include.