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Formation path of δ hydrides in zirconium by multiphase field modeling

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ABSTRACT

A multiphase field model is developed to study the effects of metastable ζ and γ hydrides on the nucleation and growth of the stable δ hydrides in α zirconium matrix. The model incorporates all the possible phases using the Gibbs free energies of formation for each phase and their available material properties. The multiphase field model is constructed by utilizing one conserved phase-field variable to represent the concentration of hydrogen, and six non-conserved phase-field variables to represent the α phase, ζ phase, three orientation variants of γ phase, and δ phase. The evolution equations are coupled with the mechanical equilibrium equations and solved using the Multiphysics Object Oriented Simulation Environment (MOOSE). Nucleation of hydrides is controlled using classic nucleation theory, inserting nuclei randomly with a probability dependent on the competition between the hydride's volume free energy and the interface's area free energy to form critical sized nuclei. The comparison between the results of the multiphase model and a two-phase model (without metastable phases) indicate that the intermediate phases are influential in the initial formation and evolution of δ phase hydrides. Random seed simulations, both in the basal plane and the $(10\bar{1}0)$ plane, also indicate that the intermediate metastable phases play a key role in the shape evolution of δ hydrides. Results suggest that quantitative phase field models of δ hydride growth need to include intermediate phases in order to accurately predict the morphology of hydrides.

1. Introduction

Zirconium based alloys are commonly used as nuclear fuel rod claddings in commercial nuclear power generation. These alloys are used due to their low neutron absorption cross section of Zr and high ductility. Among the most important weaknesses of Zr alloys is their affinity for Hydrogen, resulting in formation of hydrides in the cladding, creating brittle sections, and leading to mechanical failure. In a recent review article, we summarized the experimental and computational efforts done during the last several decades to study the hydride formation mechanisms in the cladding material [1]. One of the major weaknesses in this area is that the previous studies did not consider all the possible metastable and stable phases that could affect the hydride formation in Zr.

The four recognized phases of hydrides which can form in Zr are the metastable ζ (Zr_2H) and γ (ZrH) phases, and the stable δ ($ZrH_{1.5+x}$) and ε (ZrH_2) phases. Since ε phase is only seen at high Hydrogen concentrations and not seen in reactor operation, very little research has been done on ε phase. Some experimental researches were completed on the γ phase, with several studies on the conditions necessary to form γ hydrides and some recent arguments concerning the stability of the phase [2–6]. In general, γ hydrides are still considered to be unstable with some possible special circumstances leading to a δ to γ transformation [1]. The ζ phase was only discovered in 2008 by Zhao et al. [7], and it has been postulated to be potentially important in the formation and growth of the more stable phases [7–10]. δ phase is the most prevalent phase in nuclear fuel cladding materials. It is difficult to experimentally determine the effects of the metastable phases on the formation and growth of δ hydrides due to the short time scales of the transformations. Computational modeling can provide insights into the evolution of microstructures over these small time scales and can show the potentially important effects of the metastable phases.

Among the mesoscale models, phase field modeling has proven to be very powerful in predicting microstructural evolution in many

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material systems [1,11–17]. In recent years several studies of various phases of hydrides have been done utilizing different phase field models [7–10,18–27]. Most of these models were created for the ζ phase [7–10] and the γ phase [19–25,27], and there is only one study on the δ phase [18]. This is in spite of the fact that δ hydrides are the most commonly seen in claddings and are most detrimental to the mechanical properties of the cladding [1,28]. The works on the ζ and γ phases have cited the possibility that the intermediate phases could be important to the formation and evolution of the δ phase. It is clear that the previous phase field models need improvement in order to predict the effects of intermediate phases on the formation path and shape of stable hydrides.

Due to the lack of studies on phase field modeling of the δ phase and the possibility that the metastable phases can have some important effects on the formation and morphology of δ hydrides, this work proposes a multiphase field model which includes three phases of hydrides. This multiphase field model uses all the available material properties from computational or experimental sources. It is important to note, as it was previously stated by others, that not all the interfacial energies between phases are available and thus some approximations or lower length scale simulations must be performed [18,19]. Despite this shortcoming, this new multiphase field model is the first model to include the effects of metastable phases on the nucleation and growth of the δ phase.

2. Multiphase field model

To construct the free energy functional of the multiphase field model, one conserved phase field variable, C, is used to follow the hydrogen concentration, and six non-conserved structural field variables, η_i, are used to represent α-Zr, ζ-Zr_2H, δ-$ZrH_{1.5+x}$, and the three eigenstrain variants of γ-ZrH. The total free energy of the system is defined as the summation of the chemical free energy and the elastic free energy:

$$F = F_C + F_{el}, \tag{1}$$

where F_C is the total chemical free energy and F_{el} is the elastic free energy as follows:

$$F_C = \int_V \left[f(C, \eta_i, T) + \sum_{i,j}^{n} \frac{K_{ij}}{2} |\nabla \eta_i| \left|\nabla \eta_j\right| \right] \mathrm{d}\vec{r}, \tag{2}$$

$$F_{el} = \frac{1}{2} \int_V \sigma_{ij} \varepsilon_{ij}^{el} \mathrm{d}\vec{r} = \frac{1}{2} \int_V C_{ijkl} \varepsilon_{kl}^{el} \varepsilon_{ij}^{el} \mathrm{d}\vec{r}, \tag{3}$$

$$\begin{aligned} \varepsilon_{ij}^{el}(\vec{r}) &= \varepsilon_{ij}^{tot}(\vec{r}) - \varepsilon_{ij}^{00}(\vec{r}) = \varepsilon_{ij}^{tot}(\vec{r}) - \sum_{n=1}^{6} \varepsilon_{ij}^{00}(n) \eta_n^2(\vec{r}) \\ &= \frac{1}{2} \left(\frac{\partial u_i(\vec{r})}{\partial r_j} + \frac{\partial u_j(\vec{r})}{\partial r_i} \right) - \sum_{n=1}^{6} \varepsilon_{ij}^{00}(n) \eta_n^2(\vec{r}), \end{aligned} \tag{4}$$

where f is the chemical free energy density of the bulk, K_{ij} is gradient energy coefficient which is related to the interfacial free energy between the matrix and precipitates, T is the temperature in Kelvin, σ_{ij} is the generated stresses, C_{ijkl} is the elasticity tensor, ε_{ij}^{el} is the elastic strain, ε_{ij}^{00} is the stress free transformation strain (eigenstrain) for each orientation variable, $n = \alpha$, ζ, γ_1, γ_2, γ_3, δ, considering the corresponding values for each phase, and u_i are the displacements. In this model all the interfaces are controlled through the non-conserved order parameters. The non-conserved field variables also control the orientation of the γ phase (three orientations for γ hydrides), and the elasticity for the entire system through enforcing different eigenstrains for different phases (last term in Eq. (4)).

A recent paper by Christensen et al. [29] contains Gibbs free energies as calculated using an ab initio method for each of the hydride phases. These free energies of formation are used in our multiphase field model to control the chemical bulk free energy:

$$\Delta G_\zeta = 19.65 - 0.0231T \left[\frac{kJ}{mol} \right], \tag{5}$$

$$\Delta G_\gamma = 39.47 - 0.0351T \left[\frac{kJ}{mol} \right], \tag{6}$$

$$\Delta G_\delta = 46.37 - 0.0414T \left[\frac{kJ}{mol} \right], \tag{7}$$

where ΔG_ζ, ΔG_γ, ΔG_δ are the Gibbs free energies of formation of each respective hydride phase. These free energies are incorporated into a double well polynomial to create a chemical free energy density of the bulk in MOOSE:

$$f(C, \eta_i, T) = \left[\sum_i^n h_i(\eta_i) F_i \right] + g(\eta_i) + pk(\eta_i), \tag{8}$$

$$g(\eta_i) = \sum_{i,j,k,l}^{n} \left[(W_{kl} h_k(\eta_k) + W_{lk} h_l(\eta_l)) \eta_k^2 \eta_l^2 + A \eta_i^2 \eta_j^2 \eta_k^2 \right], \tag{9}$$

$$k(\eta_i) = \left(\left[\sum_i^n h_i(\eta_i) \right] - 1 \right)^2, \tag{10}$$

$$F_\alpha = A_\alpha (C - C_\alpha)^2, \tag{11}$$

$$F_\zeta = \Delta G_\zeta \left(A_\zeta \left(C - C_\zeta \right)^2 - 1 \right), \tag{12}$$

$$F_\gamma = \Delta G_\gamma \left(A_\gamma (C - (C_\gamma + 0.05))^2 - 1 \right), \tag{13}$$

$$F_\delta = \Delta G_\delta \left(A_\delta (C - C_\delta)^2 - 1 \right), \tag{14}$$

where C_α is the concentration of maximum hydrogen solubility in the matrix before precipitation occurs, and C_ζ, C_γ, and C_δ are the concentrations of hydrogen in the hydride phases. The constants inserted into Eqs. (11)–(14) (A_α, A_ζ, A_γ, and A_δ) control the bulk contribution to the interfacial energy as well as the tangents between the phases; these constants were determined to construct the common tangent lines between different Gibbs free energy curves of the three hydride phase and the α Zr matrix. A total of six common tangent lines are needed: α–ζ, α–δ, α–γ, ζ–γ, δ–γ, and ζ–δ tangent lines. In order to control the interface energy the $g(\eta_i)$ is added to the bulk free energy with W_{ij} controlling the barrier height, and A chosen to be large enough to prevent three phases from coexisting in any given point. $k(\eta_i)$ is a constraint which is forced to be 0 in order to ensure that the total weight of all phase free energy contributions is unity. This constraint is achieved through the use of a free energy penalty p which forces the bulk free energy of the system to increase when the constraint function is not satisfied.