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A CONTINUUM THEORY FOR EVALUATING THE IMPACT OF STRESS ON THE KINETICS OF HYDROGEN UPTAKE AND RELEASE IN METAL HYDRIDES

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Abstract. *Metal hydrides show promise as solid-state hydrogen storage options, but their practical use is challenging due to slow hydrogen uptake and release. This has led to interest in using metal nanoparticles as advanced materials for new hydrogen storage systems, as they display fast kinetics. However, understanding the adsorption and release kinetics requires an investigation of the role of stress in accommodating the misfit between metal and hydride phases. In this paper, we present a continuum theory to assess how misfit stress affects the kinetics of hydride formation and growth in metallic nanoparticles, which we then apply to study the kinetics of adsorption and release in spherical particles.*

Keywords: *diffusion-induced stress, configurational forces, hydrogen-storage systems, phase transformation*

1. INTRODUCTION

Despite being considered promising candidates for solid-state hydrogen storage, metallic materials like palladium and magnesium face challenges in practical applications due to the slow kinetics of hydrogen absorption and release Berube *et al.* (2007). This limitation has led to numerous investigations on understanding the underlying physical processes.

Several key steps are involved in hydrogen absorption by metals, including hydrogen uptake from the environment, bulk diffusion within the metal, and phase transformation Delmelle *et al.* (2015). Initially, the metal takes up hydrogen from its surroundings. This absorbed hydrogen then undergoes bulk diffusion within the metal, moving through its lattice structure. As the chemical potential increases, the hydrogen dissolves in the metal until a solubility limit is reached. A phase transformation occurs at this point, forming a hydride phase with a higher hydrogen content. These processes collectively contribute to the overall kinetics of hydrogen absorption and release in metallic materials Cheng *et al.* (1998).

Identifying the kinetic process responsible for this characteristic is crucial to overcome the limitation of slow hydrogenation and dehydrogenation kinetics. By identifying and studying the underlying factors affecting the hydrogen uptake and release rate, researchers can develop strategies to improve the efficiency and practicality of solid-state hydrogen storage in metallic materials Fortier *et al.* (2009). For example, the role of stress on the kinetics of hydrogen absorption and release has been investigated. Stress can affect the growth of hydrides in metals, and understanding its influence can provide insights into optimizing the kinetics of hydride reactions. Furthermore, the study by Khan *et al.* (2020) provides insights into the role of stress in the kinetics of hydrogen absorption and desorption. The presence of internal stress/strain fields in the MgH2-In composite suggests that stress effects can significantly improve the desorption properties of hydrogen storage materials. This aligns with the work of Duda and Tomassetti (2016, 2015), who investigated the influence of stress on the kinetics of hydride formation and growth in metals.

In the aforementioned works, Duda and Tomasseti developed a continuum model to assess the role played by stress on the kinetics of hydrogen absorption and release Duda and Tomassetti (2016, 2015). The model considered the following steps: hydrogen uptake/release on the metal-environment boundary, bulk diffusion, and phase transformation, with the latter two, assumed to be very fast in comparison with phase transformation. The continuum theories developed by Duda and Tomassetti (2016, 2015), and extended by Souza *et al.* (2018) to account for stress-dependent hydrogen mobility.

This issue has been addressed in the literature (e.g., Zhdanov (2010); Grönbeck and Zhdanov (2011)), and has provided valuable insights into the kinetics of phase transformation in metallic materials. These theories consider the influence of misfit stress and stress-dependent hydrogen mobility, allowing for a comprehensive understanding of the hydrogen absorption and release processes. By assuming the existence of a sharp and coherent interface between different phases, these models enable analytical solutions and facilitate the study of phase transformation kinetics in spherical geometries.

In this paper, we build upon the previous work by Souza *et al.* (2018) by relaxing the assumption that hydrogen uptake by the boundary occurs very rapidly. Instead, we introduce a modified boundary condition that relates the influx of hydrogen to the difference in chemical potential, similar to the convection boundary condition in heat transfer. This approach, as demonstrated by Duda *et al.* (2021), ensures thermodynamic consistency and provides a more accurate description of the hydrogen absorption process.

The paper is organized as follows. In Section 2, we revisit and expand upon the theory proposed by Souza et al. Souza *et al.* (2018), incorporating the newly introduced boundary condition for the hydrogen flux. This enhanced model provides a more comprehensive understanding of the kinetics involved. In the subsequent section, we apply the generalized theory to investigate the specific kinetics of the $\alpha - \beta$ transition in spherical particles.

Within this paper, we consistently utilize the standard notation of continuum mechanics. Symbols are defined by their first appearance to facilitate understanding and reference throughout the text.

2. THE CONTINUUM MODEL

Let us consider a body $\mathcal{B}$ that can exchange hydrogen atoms with the environment, characterized by a hydrogen chemical potential μ_{env}. Under equilibrium conditions, the hydrogen content of $\mathcal{B}$, represented by the hydrogen number density c, is determined by solving the constitutive equation $\mu = \psi'(c)$ for the hydrogen chemical potential μ, where ψ is the chemical free energy density, and the equilibrium condition $\mu = \mu_{env}$. Thus, the hydrogen content is obtained by solving the equation $\psi'(c) = \mu_{env}$, which may have multiple solutions depending on the convexity properties of ψ, indicating the possibility of multiple phases. In this discussion, we focus on situations where c_α, c_β, and μ_{eq} satisfy the following conditions:

$$\psi'(c_\alpha) = \psi'(c_\beta), \quad \psi'(c_\alpha) = \frac{\psi(c_\alpha) - \psi(c_\beta)}{c_\alpha - c_\beta}, \quad \mu_{eq} = \psi'(c_\alpha), \tag{1}$$

where c_α and c_β, with $c_\alpha > c_\beta$, represent the equilibrium hydrogen contents at the same environmental chemical potential $\mu_{env} = \mu_{eq}$. These solutions correspond to the coexistence of two phases, the α and β phases, which are equally stable without stress. We refer to μ_{eq} as the transition chemical potential.

In our investigation, we focus on the situation where the body $\mathcal{B}$ transitions from the α (β) phase to the β (α) phase. This phase transition occurs through the nucleation and propagation of an interface that separates the two phases until the transition is complete. Following the approach presented in Souza *et al.* (2018), we consider the elastic body $\mathcal{B}$ to be divided into two distinct regions: $\mathcal{B}_\alpha(t)$ and $\mathcal{B}_\beta(t)$, corresponding to the α and β phases, respectively. The interface $\mathcal{S}(t)$ dynamically evolves and demarcates the boundaries between these regions, as shown in Fig. 1.

In addition, we discuss a theory that accurately describes small deviations from the transition state. This theory involves bulk and interface equations that govern the displacement field $\mathbf{u}$, the hydrogen chemical potential μ, and the interface $\mathcal{S}(t)$. Appropriate boundaries and initial conditions must be specified to fully define the system. In the upcoming subsections, we will introduce the governing equations and discuss the necessary boundary and initial conditions for these equations.

2.1 Bulk conditions

The bulk equations of the theory are derived by combining the force and hydrogen-content balances with a constitutive theory. These equations can be expressed as

$$\operatorname{div} \mathbf{T} = \mathbf{0} \quad \text{and} \quad -\operatorname{div} \mathbf{h} = \dot{c}, \tag{2}$$

where div is the divergence operator, $\mathbf{T}$ is the Cauchy stress tensor, and $\mathbf{h}$ is the solute flux vector. Body forces, inertia, and solute supply have been neglected in these equations.

In addition to the balances mentioned above, it is crucial to consider an energy imbalance equation, which at the local level in bulk, can be expressed as

$$\dot{\omega} - \mathbf{T} \cdot \dot{\mathbf{E}} + c\dot{\mu} - \mathbf{h} \cdot \nabla\mu \leq \mathbf{0}, \tag{3}$$

where $\dot{\omega}$ represents the rate of change of the grand canonical potential density, $\mathbf{E}$ is the symmetric part of the gradient of the displacement field $\mathbf{u}$, μ is the chemical potential, and $\nabla\mu$ represents its gradient.

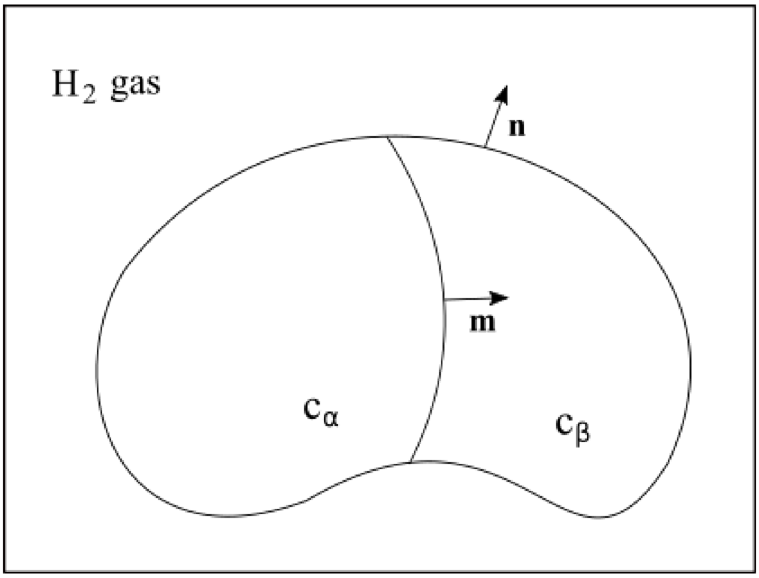

Figure 1. Two-phase metal-hydride system in a hydrogen gas environment.

The form of the energy imbalance equation (3) is appropriate for formulating a constitutive theory in which the chemical potential, rather than the concentration, is treated as an independent constitutive variable and hence a primary variable of the theory. This is the case under study here, focusing on small departures from the transition chemical potential. The equation captures the energy imbalance associated with these deviations and provides a fundamental framework for understanding the system's behavior in response to changes in the chemical potential.

2.2 Interface conditions

The interface conditions are obtained by localizing the force and solute-content balance, as well as the free-energy inequality at the $\alpha - \beta$ interface, based on the following assumptions: the interface is coherent and local chemical equilibrium prevails during its evolution, meaning that the displacement $\mathbf{u}$ and chemical potential μ are continuous across the interface; it propagates without dissipation, leading to the validity of the Maxwell condition therein. These interface conditions can be expressed as:

- Continuity of the displacement and chemical potential

$$[|\mathbf{u}|] = \mathbf{0}, \qquad [|\mu|] = 0, \tag{4}$$

- Force and solute content balances

$$[|\mathbf{T}|]\mathbf{m} = \mathbf{0}, \qquad [|c|]v - [|\mathbf{h}|] \cdot \mathbf{m} = 0, \tag{5}$$

- Maxwell relation

$$[|\omega - (\nabla \mathbf{u})\mathbf{m} \cdot \mathbf{T}\mathbf{m}|] = 0. \tag{6}$$

where $[|A|] = (A_\beta - A_\alpha)$ denotes the jump in a field A across the interface, and v is the velocity of the interface in the direction of the unit vector $\mathbf{m}$.

2.3 Boundary conditions

We consider $\partial\mathcal{B}$ immersed in a reservoir of hydrogen gas at pressure p. Under the standard assumption that the gas pressure can be neglected from the mechanical point of view, the mechanical boundary condition can be simplified as follows:

$$\mathbf{T}\mathbf{n}|_{\partial\mathcal{B}} = \mathbf{0}. \tag{7}$$

where $\mathbf{n}$ is unit outward normal vector field on $\partial\mathcal{B}$.

As for the chemical boundary condition, the study by Souza *et al.* (2018) considered that local chemical equilibrium prevailed at the boundary. This condition is given by

$$\mu = \mu_R = \frac{1}{2}\mu_{H_2}, \tag{8}$$

where μ_R is the solute chemical potential in the reservoir, and μ_{H_2} is the chemical potential of gaseous hydrogen given by $\mu_{H_2} = \mu^0_{H_2} + k_B T \ln\frac{p}{p_0}$, where $\mu^0_{H_2}$ is the chemical potential of gaseous hydrogen at the reference pressure p_0.

Here, we deviate from the local chemical equilibrium boundary condition (8) by considering a different boundary condition given by

$$\mathbf{h}\cdot\mathbf{n} = \varpi(\mu - \mu_R) \tag{9}$$

on the solute entry, where $\varpi > 0$. This boundary condition is consistent with thermodynamics, as discussed in Duda *et al.* (2021). It can be shown that the local chemical equilibrium boundary condition (8) can be obtained in the limit as ϖ goes to infinity.

2.4 Constitutive equations

Based on the dissipation inequality (3), we propose constitutive equations for ω, $\mathbf{T}$, c, and $\mathbf{h}$ in terms of $\mathbf{E}$, μ, and $\nabla\mu$. By following the Coleman-Noll procedure, we find that the following conditions must hold:

$$\omega = \hat{\omega}_\phi(\mu, \mathbf{E}), \qquad c = -\frac{\partial\,\hat{\omega}_\phi(\mu, \mathbf{E})}{\partial\mu}, \qquad \mathbf{T} = \frac{\partial\,\hat{\omega}_\phi(\mu, \mathbf{E})}{\partial\mathbf{E}}, \qquad \mathbf{h} = -\hat{\mathbf{M}}_\phi(\mu, \mathbf{E}, \nabla\mu)\nabla\mu. \tag{10}$$

The response function $\hat{\mathbf{M}}_\phi$ is a positive semidefinite tensor-valued function. From a constitutive perspective, the theory is defined by the response functions $\hat{\omega}_\phi$ and $\hat{\mathbf{M}}_\phi$, which consist of four constitutive functions, two for phase α and two for phase β.

We present a constitutive specialization suitable for describing situations involving small deviations of the transition chemical potential μ_{eq} at which the phases α and β coexist in a stress-free and stable equilibrium, with the corresponding solute content densities given by c_α and c_β, where $c_\beta > c_\alpha$. This theory is based on the following assumption:

- Additive decomposition of the total strain $\mathbf{E}$ into its elastic part $\mathbf{E}_e$ and its stress-free part $\mathbf{E}_{0\phi}$, at phase ϕ

  $$\mathbf{E} = \mathbf{E}_e + \mathbf{E}_{0\phi}, \quad \mathbf{E}_{0\phi} = \hat{\epsilon}_\phi(c_\phi)\mathbf{I}, \quad \text{with} \quad \hat{\epsilon}_\alpha(c_\alpha) = \eta_\alpha(c_\alpha - c_{0\,\alpha}) \quad \text{and} \quad \hat{\epsilon}_\beta(c_\beta) = \eta_\beta(c_\beta - c_{0\,\beta}) + e_T \tag{11}$$

  where e_T is the transformation strain, $c_{0\phi}$ is a reference value of the solute content in the ϕ-phase for measuring the strain, η_ϕ is a material parameter. We define the misfit strain between the β and α phases

  $$\epsilon_0 = \hat{\epsilon}_\beta(c_\beta) - \hat{\epsilon}_\alpha(c_\alpha). \tag{12}$$

- The grand canonical potential takes on the following specific form:

  $$\hat{\omega}_\phi(\mu, \mathbf{E}) = -c_\phi\,(\mu - \mu_{eq}) + \frac{\lambda}{2}(\mathrm{tr}\,\mathbf{E}_e)^2 + G|\mathbf{E}_e|^2, \tag{13}$$

  where λ and G represent the Lamé elastic moduli, assumed to be the same for both phases.

- The response function $\hat{\mathbf{M}}_\phi$ is allowed to depend on the stress $\mathbf{T}$ and solute content c. Therefore, we consider the isotropic specialization given by

  $$\hat{\mathbf{M}}_\phi(c_\phi, \mathbf{T}) = m_\phi f_\phi c_\phi \mathbf{I} \qquad \text{where} \qquad f_\phi = \hat{f}_\phi(\mathrm{tr}\,\mathbf{T}) = \exp\left(\frac{(\eta_{*\,\phi} - \eta_{0\,\phi})\mathrm{tr}\,\mathbf{T}}{3k_B T}\right), \tag{14}$$

  where m_ϕ is the stress-free solute mobility and $f_\phi = \hat{f}_\phi(\mathrm{tr}\,\mathbf{T}) > 0$ accounts for the stress effect on the solute mobility through the trace of the stress tensor $(\mathrm{tr}\,\mathbf{T})$. For instance, if one accounts for the stress-dependency of the activation energy for diffusion, it can be shown that $\hat{f}_\phi(\mathrm{tr}\,\mathbf{T})$ can be given by(14), according to Grönbeck and Zhdanov (2011), where $\eta_{0\,\phi}(\eta_{*\,\phi})$ is the volume occupied by a solute atom in its ground (activated) state, k_B the Boltzmann constant, and T the absolute temperature.

From $(10)_2$ and (13) we have

$$c = \begin{cases} c_\alpha & \text{in } \mathcal{B}_{\alpha(t)}, \\ c_\beta & \text{in } \mathcal{B}_{\beta(t)}, \end{cases} \tag{15}$$

thereupon the solute content density c is a piecewise-homogeneous field, and hence $\dot{c} = 0$ in bulk. From $(10)_3$ and (13) the stress tensor $\mathbf{T}$ is given by

$$\mathbf{T} = \lambda\,(\operatorname{tr}\mathbf{E}_e)\mathbf{I} + 2G\,\mathbf{E}_e \qquad \text{with} \qquad \mathbf{E}_e = \begin{cases} \mathbf{E} - \hat{\epsilon}_\alpha(c_\alpha)\,\mathbf{I} & \text{in } \mathcal{B}_{\alpha(t)}, \\ \mathbf{E} - \hat{\epsilon}_\beta(c_\beta)\,\mathbf{I} & \text{in } \mathcal{B}_{\beta(t)}. \end{cases} \tag{16}$$

From $(10)_4$ and (14) the solute flux $\mathbf{h}$ is given by

$$\mathbf{h} = \begin{cases} -m_\alpha f_\alpha c_\alpha \nabla\mu & \text{in } \mathcal{B}_\alpha(t) \\ -m_\beta f_\beta c_\beta \nabla\mu & \text{in } \mathcal{B}_\beta(t). \end{cases} \tag{17}$$

2.5 Summary of the governing equations

We now summarize the governing equations of the theory under consideration for the moving boundary-initial value problem. The unknowns fields are: $\mathbf{u}(\mathbf{x},t), \mu(\mathbf{x},t), \mathcal{S}(t)$

- Displacement field $\mathbf{u}$

$$\begin{aligned} &\operatorname{div}\mathbf{T} = \mathbf{0} \quad \text{and} \quad \mathbf{T} = \lambda\,(\operatorname{tr}\mathbf{E}_e)\mathbf{I} + 2G\,\mathbf{E}_e \qquad \text{on} \quad \mathcal{B}|\mathcal{S}(t) \\ &[|\mathbf{u}|] = \mathbf{0} \quad \text{and} \quad [|\mathbf{T}|]\mathbf{m} = \mathbf{0} \quad \text{on} \quad \mathcal{S}(t) \quad \text{and} \quad \mathbf{T}\mathbf{n} = \mathbf{0} \qquad \text{on} \quad \partial\mathcal{B} \end{aligned} \tag{18}$$

- Chemical potential field μ

$$\begin{aligned} &\operatorname{div}\mathbf{h} = 0 \quad \text{and} \quad \mathbf{h} = -m\nabla\mu \qquad \text{on} \quad \mathcal{B}|\mathcal{S}(t) \\ &[|\mu|] = 0 \quad \text{and} \quad [|\omega - (\nabla\mathbf{u})\mathbf{m}\cdot\mathbf{T}\mathbf{m}|] = 0 \qquad \text{on} \quad \mathcal{S}(t) \\ &\mathbf{h}\cdot\mathbf{n} = \varpi(\mu - \mu_R) \qquad \text{on} \quad \partial\mathcal{B} \end{aligned} \tag{19}$$

- Moving interface $\mathcal{S}$

$$\begin{aligned} &[|c|]v = [|\mathbf{h}|]\cdot\mathbf{m} \qquad \text{on} \quad \mathcal{S}(t) \quad \text{with} \quad \mathcal{S}(0) = \mathcal{S}_0 \\ &\mathbf{E}_e = \mathbf{E} - \hat{\epsilon}_\phi(c_\phi)\mathbf{I}, \quad \omega = -c_\phi(\mu - \mu_{eq}) + \frac{\lambda}{2}(\operatorname{tr}\mathbf{E}_e)^2 + G|\mathbf{E}_e|^2, \quad m = m_\phi f_\phi c_\phi \end{aligned} \tag{20}$$

3. SPHERICAL GEOMETRY

Let us now consider that $\mathcal{B}$ is a solid sphere of radius R, divided into two phases α and β, by a concentric sharp interface $\mathcal{S}(t)$ of radius $\rho(t)$. The inner region is occupied by the α-phase, while the outer region is occupied by the β-phase

$$\mathcal{B} = \{\mathbf{x} : |\mathbf{x}| \leq R\}, \qquad \mathcal{B}_\alpha = \{\mathbf{x} : 0 \leq |\mathbf{x}| < \rho(t)\}, \qquad \mathcal{B}_\beta = \{\mathbf{x} : \rho(t) < |\mathbf{x}| \leq R\} \tag{21}$$

The concentric sharp interface and the normal velocity are

$$\mathcal{S}(t) = \{\mathbf{x} : |\mathbf{x}| = \rho(t)\}, \qquad \dot{\rho}(t) = v. \tag{22}$$

The stress, strain, and chemical potential fields are obtained from the knowledge of the current position of the interface, as will be discussed below. Thanks to the spherical symmetry of the problem, we have

$$\mathbf{u}(\mathbf{x}) = u(r)\mathbf{e}, \;\; \mathbf{e} = \frac{\mathbf{x}}{|\mathbf{x}|}, \;\; \mu(\mathbf{x}) = \mu(r), \;\; r = |\mathbf{x}|, \;\; \mathbf{E} = u'\mathbf{e}\otimes\mathbf{e} + \frac{u}{r}(\mathbf{I} - \mathbf{e}\otimes\mathbf{e}), \;\; \mathbf{T} = \sigma_r\,\mathbf{e}\otimes\mathbf{e} + \sigma_\theta(\mathbf{I} - \mathbf{e}\otimes\mathbf{e}) \tag{23}$$

where a' denotes $(\mathrm{d}a/\mathrm{d}r)$.

According to the equations (16) and (23), the stress components are then given by

$$\begin{aligned} \sigma_r(r)_\phi &= 2\lambda\Big(\frac{u(r)}{r} - u'(r)\Big) + 3\kappa\Big(u'(r) - \hat{\epsilon}_\phi(c_\phi)\Big), \\ \sigma_\theta(r)_\phi &= -\lambda\Big(\frac{u(r)}{r} - u'(r)\Big) + 3\kappa\Big(\frac{u(r)}{r} - \hat{\epsilon}_\phi(c_\phi)\Big), \\ \operatorname{tr}\mathbf{T}(r)_\phi &= 3\kappa\Big(2\frac{u(r)}{r} + u'(r) - 3\hat{\epsilon}_\phi(c_\phi)\Big), \end{aligned} \tag{24}$$

where $3\kappa = 2G + 3\lambda$ is the bulk modulus.

Taking (24) into account, the force balance described in $(2)_1$ can be rewritten as

$$\frac{d}{dr}\left(\frac{1}{r^2}\frac{d}{dr}\Big(r^2u(r)\Big)\right)=0, \tag{25}$$

which general solution is given by

$$u(r)=\begin{cases} C_1^{\alpha}r \quad \text{for} \quad 0\le r\le\rho, \\ C_1^{\beta}r+\dfrac{C_2^{\beta}}{r^2} \quad \text{for} \quad \rho\le r\le R. \end{cases} \tag{26}$$

From conditions $(4)_1$, $(5)_1$ and (7), we have

$$\begin{aligned} C_1^{\alpha}&=\hat{\epsilon}_{\alpha}(c_{\alpha})-\frac{\epsilon_0}{3\,(2G+\lambda)}\left(3\kappa+4G\left(\frac{\rho}{R}\right)^3\right), \\ C_1^{\beta}&=\hat{\epsilon}_{\beta}(c_{\beta})-\frac{4G\epsilon_0}{3\,(2G+\lambda)}\left(\frac{\rho}{R}\right)^3, \\ C_2^{\beta}&=-\frac{\kappa\epsilon_0\rho^3}{(2G+\lambda)}. \end{aligned} \tag{27}$$

where ϵ_0, from (12), represents the misfit strain between the β and α phases.

We now consider the determination of the chemical potential. From $(24)_3$ and (26), $\operatorname{tr}\mathbf{T}$ is piecewise homogeneous and hence μ is harmonic in bulk. This implies that $\mu(r)$ satisfies the equation

$$\frac{d}{dr}\left(r^2\frac{d}{dr}\mu(r)\right)=0, \tag{28}$$

the general solution of which is given by

$$\mu(r)=\begin{cases} D_1^{\alpha} \quad \text{for} \quad 0\le r\le\rho, \\ D_1^{\beta}+\dfrac{D_2^{\beta}}{r} \quad \text{for} \quad \rho\le r\le R. \end{cases} \tag{29}$$

From conditions $(4)_2$, (9) and (6), we have

$$\begin{aligned} D_1^{\alpha}&=\mu(\rho)=\mu_{eq}+\mu_0\left(2\left(\frac{\rho}{R}\right)^3-1\right)=:\mu_{\rho}, \\ D_1^{\beta}&=\mu_R-(1-\zeta)\left(\frac{\rho}{R-(1-\zeta)\rho}\right)(\mu_R-\mu_{\rho}), \\ D_2^{\beta}&=\left(\frac{\rho R}{R-(1-\zeta)\rho}\right)(\mu_{\rho}-\mu_R), \end{aligned} \tag{30}$$

$$\text{where} \qquad \zeta=\frac{m_{\beta}c_{\beta}f_{\beta}(\operatorname{tr}\mathbf{T})}{\varpi R}, \quad \operatorname{tr}\mathbf{T}=9\kappa\big(C_1^{\beta}-\hat{\epsilon}_{\beta}(c_{\beta})\big) \quad \text{and} \quad \mu_0=\frac{6G\,\kappa\,\epsilon_0^2}{(2G+\lambda)(c_{\beta}-c_{\alpha})}. \tag{31}$$

As ϖ approaches infinity, ζ goes to zero, leading to the results obtained by Souza *et al.* (2018), as mentioned earlier. From (29) and (30) we obtain

$$\mu'(r)=\begin{cases} 0 \quad \text{for} \quad 0\le r\le\rho, \\ \left(\dfrac{\mu_R-\mu_{\rho}}{R-(1-\zeta)\rho}\right)\dfrac{\rho R}{r^2} \quad \text{for} \quad \rho\le r\le R. \end{cases} \tag{32}$$

4. THE EVOLUTION OF THE INTERFACE

We now obtain the evolution equation of the interface. From $(5)_2$, (17) and (32) we have

$$\dot{\rho}(t)=\frac{m_{\beta}f_{\beta}(\operatorname{tr}\mathbf{T})c_{\beta}}{c_{\beta}-c_{\alpha}}\left(\frac{\mu_{\rho}-\mu_R}{R-(1-\zeta)\rho}\right)\frac{R}{\rho}. \tag{33}$$

It is important to recall that (33) was derived under the assumption that the α-phase occupies the inner core of the sphere. However, if the β-phase occupies the inner core, the variables c_{α} and c_{β} should be replaced by c_{β} and c_{α}, respectively.

Using (14), the equation (33) can be rewritten as

$$\tau\big(1-(1-\zeta)y\big)y\,\dot{y}=\exp\left(Ay^3\right)\big(B\left(2y^3-1\right)-1\big) \tag{34}$$

$$\text{where} \qquad y=\frac{\rho}{R}, \quad \tau=\left(\frac{c_\beta-c_\alpha}{c_\beta}\right)\frac{R^2}{m_\beta\left(\mu_R-\mu_{eq}\right)}, \quad A=\frac{4\kappa G\epsilon_0}{(2G+\lambda)}\frac{\left(\eta_{0\beta}-\eta_{*\beta}\right)}{k_BT}, \quad \text{and} \quad B=\frac{\mu_0}{\mu_R-\mu_{eq}}. \tag{35}$$

Notice that τ is a characteristic time associated with the phase transition in the absence of stress.

We seek solutions of Equation (34) with the initial conditions $y(0)=1$ and $\dot{y}<0$. This scenario corresponds to the initial stage of the process where the sphere is predominantly in the α-phase. The β-phase begins nucleating at the boundary, and the interface moves towards the sphere's interior. This process is called the $\alpha\rightarrow\beta$ transformation or absorption process. On the other hand, if the specimen is initially saturated, meaning $y(0)=0$, indicating that the entire sphere is in the β-phase, and if the process continues with $\dot{y}>0$, the α-phase starts nucleating at the boundary. This process is called the $\beta\rightarrow\alpha$ transformation or desorption process.

By analyzing Equation (34), one can determine the necessary conditions for the occurrence of phase transformations and also calculate the required time for the transformations to take place. First, as already observed by Souza *et al.* (2018), if the solid sphere is initially in the single α-phase, it will remain in that phase as long as

$$\mu_R<{\mu_R}^{\alpha\rightarrow\beta}:=\mu_{eq}+\mu_0. \tag{36}$$

The $\alpha\rightarrow\beta$ transformation takes place when

$$\mu_R={\mu_R}^{\alpha\rightarrow\beta}:=\mu_{eq}+\mu_0. \tag{37}$$

Otherwise, if the solid sphere is initially in the single β-phase, it will remain in that phase as long as

$$\mu_R>{\mu_R}^{\beta\rightarrow\alpha}:=\mu_{eq}-\mu_0. \tag{38}$$

The $\beta\rightarrow\alpha$ transformation takes place when

$$\mu_R={\mu_R}^{\beta\rightarrow\alpha}:=\mu_{eq}-\mu_0. \tag{39}$$

Therefore, the absorption/desorption cycle displays hysteresis, with a loop amplitude given by

$${\mu_R}^{\alpha\rightarrow\beta}-{\mu_R}^{\beta\rightarrow\alpha}=2\mu_0=\frac{12G\,\kappa\,{\epsilon_0}^2}{(2G+\lambda)(c_\beta-c_\alpha)}. \tag{40}$$

To calculate the required time for the transformations to reach the interface at location y, we can define the function

$$h(x)=\frac{\big(1-(1-\zeta)x\big)x}{\exp(Ax^3)\big(B\,(2x^3-1)-1\big)}. \tag{41}$$

Then, the time for the $\alpha\rightarrow\beta$ transformation to reach the location y, denoted by $\Gamma_{\alpha\rightarrow\beta}(y)$, is given by

$$\Gamma_{\alpha\rightarrow\beta}(y)=\tau\left|\int_0^y h(x)dx\right|. \tag{42}$$

In particular, the time required for the complete α-β transformation to occur is given by $\Gamma_{\alpha\rightarrow\beta}(1)$. Similarly, the $\beta\rightarrow\alpha$ transformation time, denoted by $\Gamma_{\beta\rightarrow\alpha}$, can be obtained using a similar integral expression.

Figure 2 depicts the time dependence of the volume fraction of the hydride phase, $C(t)=g\big(y(t)\big)$, where

$$g(y)=\frac{(1-y^3)c_\beta}{y^3c_\alpha+(1-y^3)c_\beta} \tag{43}$$

during the α to β transformation for $c_\beta/c_\alpha=4$, with parameters set at $A=0.0$ and $B=0.5$ and differents values of parameter ζ. When the stress does not affect the mobility (i.e., $A=0$), we find that the stress accelerates α to β transformation. However, if we consider different increasing values of dimensionless parameter ζ from zero, then the α to β transformation slows down, and the corresponding transformation time is longer in comparison to the case in which $\zeta=0.0$. To illustrate the effect of the parameter ζ on the transformation time of the hydride phase, in Fig. 3 we show the normalized transformation time ($\Gamma_{\alpha\rightarrow\beta}(1)/\tau$) against the dimensionless parameter ζ. Therefore, according to the simple model presented in this paper, stress affects the kinetics of the α to β transformation in two opposite ways, speeding up and slowing down the phase transformation. We emphasize that these results are preliminary and presented here for illustrative purposes only.

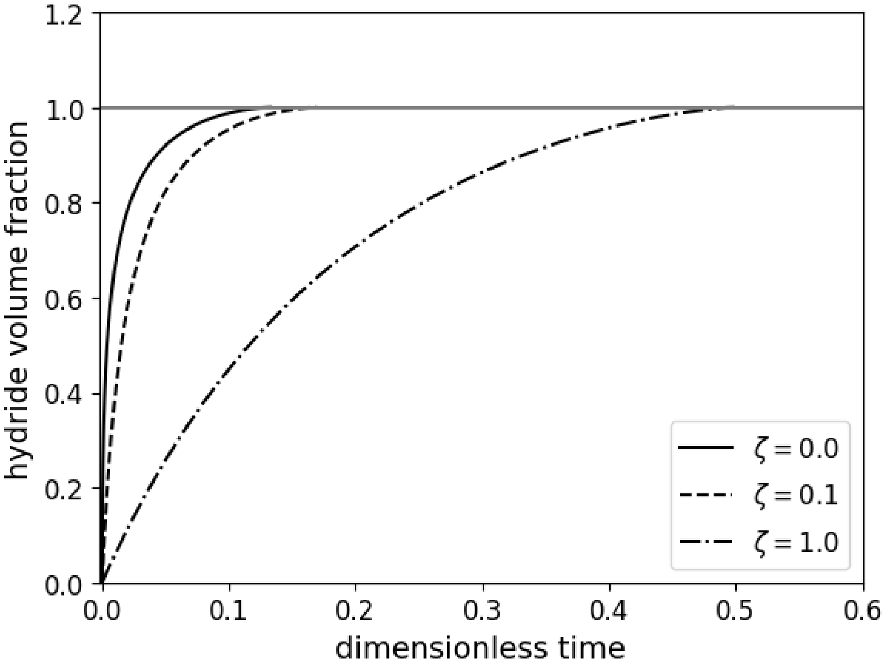

Figure 2. Evolution of hydride fraction within a sphere over dimensionless time t/τ, with parameters set at $A = 0$, $B = 0.5$, and different values of ζ

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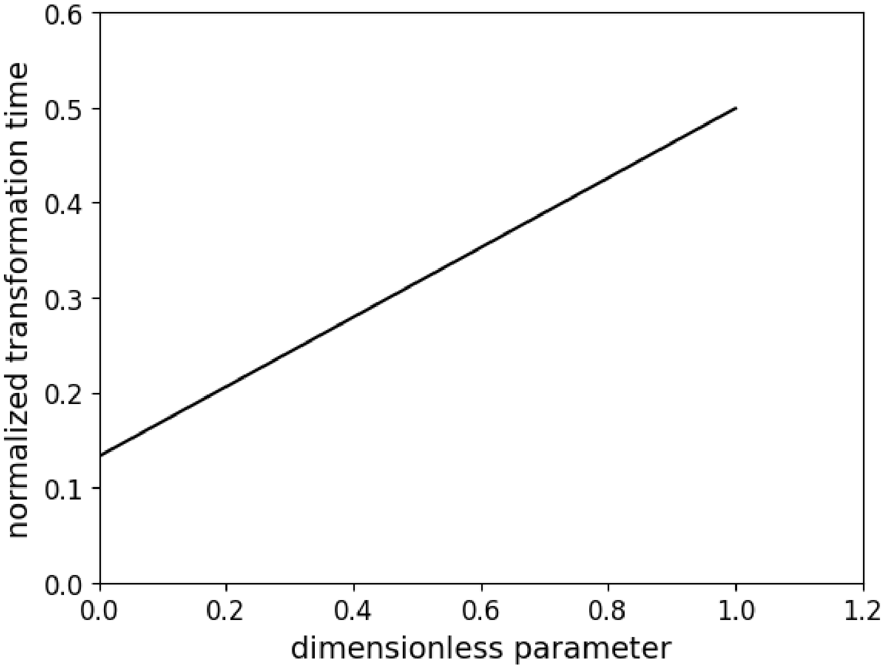

Figure 3. Normalized transformation time, $\Gamma_{\alpha\to\beta}(1)/\tau$, against the dimensionless parameter ζ.

5. CONCLUSIONS

A continuum theory was presented in this study to describe the stress effects on the kinetics of hydrogen uptake and release in metals. The theory was based on several simplifying assumptions: (1) the α/β (β/α) transformation is the rate-determining step in the absorption (desorption) of hydrogen, (2) the deviation of the hydrogen chemical potential from the transition chemical potential, at which the α and β phases would coexist in the absence of stress, is small, (3) in each of the phases, the bulk hydrogen concentration is constant and given by the corresponding value at the transition chemical potential. In addition to these considerations, a more realistic boundary condition for hydrogen inflow was analyzed in this work. This generalization extends the previous study conducted by Souza *et al.* (2018), where a continuum theory was developed to describe the stress effects on hydrogen kinetics in metals.

As an application of the theory, an analytical treatment was employed to study the kinetics of hydrogen adsorption and release in a spherical particle. The results demonstrated the presence of hysteresis, and an equation was derived to express the ratio of H_2 pressures that trigger the α/β and β/α transformations. Furthermore, it was observed that during the α/β (β/α) transformation, hydrogen diffusion slows down (speeds up) in the β (α) phase due to the presence of compressive (tensile) mean stress.

Based on these findings, it was predicted that the presence of stress delays (accelerates) the α to β (β to α) transformation. To explore more general geometries and conditions, a phase-field model of the Cahn-Hilliard type was suggested as a promising avenue for future investigation. Such a model could be calibrated using the analytical model presented in this study.

6. ACKNOWLEDGEMENTS

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