ATOMISTIC-SCALE MODEL FOR THE NUMERICAL ANALYSIS OF THE HYDROGEN DIFFUSION ON MAGNESIUM ALLOYS

M. Molinos [1*], M. Ortiz [2], M.P Ariza [1]

[1]Escuela Técnica Superior de Ingeniería, Universidad de Sevilla, Sevilla 41092, Spain
[2]Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA, 91125, United States
[*] Corresponding author: mmolinos@us.es

RESUMEN

Las aleaciones estructurales de magnesio (Mg) ofrecen propiedades deseables como baja densidad, maquinabilidad y alta resistencia específica. Estas propiedades hacen que dichas aleaciones sean ventajosas para su uso en muchas aplicaciones estructurales, pero también para aplicaciones como material de almacenamiento de hidrógeno debido al coste favorable y a las altas densidades gravimétrica y volumétrica del hidrógeno. Sin embargo, la susceptibilidad de las aleaciones de Mg a los fenómenos de fragilización por hidrógeno puede dar lugar a una baja ductilidad y tenacidad a temperatura ambiente, pudiendo dificultar sus aplicaciones potenciales. Para ello, se propone un marco teórico para la simulación de la difusión de hidrógeno en Mg basado en cálculos atomísticos utilizando Dinámica Molecular Difusiva (DMD) que nos permita estudiar el comportamiento del magnesio y sus hidruros en diferentes condiciones de presión-temperatura. Nuestro modelo resuelve un problema acoplado Termo-Chemo-Mecánico (TMC) mediante un esquema escalonado. Por un lado, la parte termo-mecánica considera un potencial ADP termalizado que es el más adecuado para modelar la transición de fase del Mg (bcc↔hcp) causada por la formación de MgH_2 a temperatura finita. Finalmente, el problema químico, que rige la evolución temporal, se resuelve mediante una ecuación de difusión calibrada con información macroscópica.

PALABRAS CLAVE: Difusión de Hidrógeno, Almacenamiento de Hidrógeno, Magnesio, Modelos atomísticos, Diffusive Molecular Dynamics

ABSTRACT

Magnesium (Mg) structural alloys offer desirable properties such as low density, machinability, and high specific strength. These properties make Mg alloys advantageous for use in many structural applications but also for applications as a hydrogen storage material due to the favorable cost and high gravimetric and volumetric densities of hydrogen. However, the susceptibility of Mg alloys to hydrogen embrittlement phenomena can lead to low ductility and low fracture toughness at room temperature, which may hinder their potential applications. Therefore, information about the behavior of magnesium and its hydrides under different pressure-temperature conditions is highly required. A theoretical framework for the simulation of hydrogen diffusion in Mg based on fully atomistic calculations using the Diffusive Molecular Dynamics (DMD) is proposed. Our model consists of the resolution of a Thermo-Chemo-Mechanical (TMC) coupled problem solved thorough a staggered scheme. On the one hand, the thermo-mechanical part considers a thermalized Angular Dependent Potential (ADP) which is best suited to model the phase transition of Mg (bcc↔hcp) caused by the formation of MgH_2 at finite temperature. And, on the other hand, the chemical problem, which drives the time evolution, is solved by a diffusion equation calibrated with macroscopic information.

KEYWORDS: Hydrogen diffusion, Hydrogen storage, Magnesium, Atomistic models, Diffusive Molecular Dynamics

1. INTRODUCTION

Solute-induced phase transformation is a key process in various energy conversion and storage applications. Magnesium (Mg) alloys offer desirable properties such as low density, machinability, and high specific strength. These properties make Mg alloys advantageous for use as hydrogen storage container. However, the susceptibility of Mg alloys to hydrogen embrittlement phenomena can lead to low ductility and low fracture toughness at room temperature, which may hinder their

potential applications, on top of that hydrogen diffusivity is not a constant, furthermore, experimental research [1]–[4] performed at fixed hydrogen composition (near Mg or near MgH_2) shown that hydrogen diffusion varies at various stages of magnesium (de)hydrogenation. Therefore, there is no doubt that information about the behavior of magnesium and its hydrides under different pressure-temperature conditions is highly required.

Numerical analysis of this phenomenon is an attractive resource in order to achieve this goal since, well

calibrated, allow us to perform a large number of numerical experiments to enhance our comprehension of the phenomenon. Continuum approaches [5]–[7] has been widely applied to simulate hydrogen diffusion in metals and its posterior embrittlement achieving good agreement with experimental results. However, they fail to account for the fine atomistic structure (*e.g.* local lattice distortion and dislocations) across the phase boundary due to its non-continuum nature. On the other hand, classical Molecular Dynamics (DM) does supply fully atomistic detail but need to resolve the thermal vibration of the atoms which takes place in range of the picoseconds, several orders of magnitude below the hydrogen diffusion process, which takes this method out of consideration [8], [9].

In this work, we apply a novel computational framework referred as diffusive molecular dynamics (DMD). This method is a new paradigm for simulating the Thermo-Chemo-Mechanical (TMC) problems while maintaining full atomic resolution. The defining idea underlying DMD is the assumption that the time scale of diffusion is much larger than that of microscopic state transitions. Therefore, at an intermediate time scale, the microscopic state variables can be considered as random variables. This allows to couple a non-equilibrium statistical thermodynamics model that supplies the requisite driving forces for kinetics with a discrete diffusion equation calibrated using macroscopic data. In comparison to the stablished atomistic models such as statistically averaged MD simulations [8], DMD has a larger simulation time window as it does not explicitly resolve thermal vibrations nor individual microscopic state transitions. The DMD has been applied to nanoindentation and sintering [10], dislocation extension [11], nanovoid growth [12], solute-defect interactions [13] and silicon lithiation [14]. A recent study by Sun et al. [9] shows that the DMD model, when equipped with an embedded atom method (EAM), can capture the separation of the α and β phases of the system palladium-hydrogen (Pd-H).

However, magnesium hydride is an example of a so-called "trans-formational" material since magnesium and magnesium hydride have different crystal structures: hexagonal closely packed (hcp) structure for Mg and tetragonal rutile structure for α-MgH$_2$ (bcc $\leftrightarrow$ hcp). This contrasts with diffusional systems such as PdH$_x$, for which palladium and palladium hydride have the same face-centered cubic (fcc) crystal structure. The main novelty of this paper in the proposal of a DMD model capable of modeling the phase transition of Mg during (de)hydrogenation at finite temperature by means of a *thermalized* Angular Dependent Potential (ADP) [15].

The structure of this paper is a follow: we begin by presenting a succinct summary of DMD in the interest of completeness, in Section 2. The thermalized ADP is subsequently presented in Section 3. A summary and concluding remarks are consigned to Section 4, by way of closing.

2. METHODOLOGY

We consider an HCP Mg sample, which includes host sites occupied by Mg atoms and interstitial hexahedral and octahedral sites that can be either occupied by H atom or unoccupied. Henceforth, we denote the sites belonging to the Mg lattice as I_{Mg}, and the interstitial sites by I_H. At each interstitial site $i \in I_H$, we introduce an occupancy function defined as

$$n_i = \begin{cases} 1 \text{ is the site } i \text{ is occupied by a H atom} \\ 0 \text{ if the site } i \text{ is unoccupied.} \end{cases}$$

(1)

The *microscopic states* of the system are defined by the occupancy array $\{n\} = (n_i)_{i \in I_H}$ and the instantaneous value of the *phase space* given by $\{z\} \equiv (q_i, p_i)_{i \in I_{Mg} \cup I_H}$, where q_i and p_i stands by position and momenta respectively. Based on the assumption of the scale separation and the ergodic hypothesis, these microscopic state variables that have a joint probability distribution characterized by the density function $\rho(z, n)$. We determine ρ by recurring to Jaynes' principle of maximum entropy [16], [17], *i.e.*, by maximizing the information-theoretical entropy to be

$$\max_{\{z\},\{n\}} S[\rho] = -k_B \langle \log \rho \rangle,$$

(2)

This system is required to fulfill the following macroscopic local restrictions

$$\begin{cases} \langle h_i \rangle = e_i, & i \in I_{Mg} \cup I_H, \\ \langle n_i \rangle = \chi_i, & i \in I_H. \end{cases}$$

(3)

Where k_B is the Boltzmann constant, and $\langle \cdot \rangle$ is an operator known as *phase average*, which applied over any function, say $A(\{z\}, \{n\})$, returns the expected or *macroscopic* value of the given function. Here, h_i denotes the local Hamiltonian, e_i is the particle energy and χ_i is the atomic fraction.

In order to impose the set of restrictions Eqns. (3) into the optimization problem enunciated by Eqn. (2), we appeal to the classical method of Lagrange multipliers, where we transform the constrain maximization problem into an *unconstrained* problem resulting in

$$\rho = \frac{1}{\Xi} e^{-\{\beta\}^T \{h\} + \{\gamma\}^T \{n\}},$$

(4)

where Ξ is the partition function, and $\{\beta\}$ and $\{\gamma\}$ are Lagrange multipliers. Eqn. (4), can be interpreted as non-equilibrium generalization of the Gibbs grand-canonical

probability density function. Notice, $T_i = \frac{1}{k_B \beta_i}$ and $\mu_i = k_B T_i \gamma_i$ can be defined as the particle absolute temperature and the chemical potential of site i, respectively. As in the equilibrium theory, it is sometimes convenient to work with the *grand-canonical free entropy* Φ, which can be obtained substituting (4) into Eqn. (2) and getting the convex conjugate of the resulting expression by the application of the Legendre transformation

$$\Phi(\{\beta\},\{\gamma\}) = \max_{\rho} \mathcal{L}[\rho,\{\beta\},\{\gamma\}] = k_B \log \Xi(\{\beta\},\{\gamma\}).$$

(5)

Because the Hamiltonian h_i is typically a nonlinear function, the calculation of the thermodynamic potentials (*e.g.*, e_i and Ξ) is generally intractable. This limitation can be surmounted by the application of a variational formulation, *e.g.* Ref. [18]. Let us define a trial energy $h_0 \in \mathcal{H}_0$, and $\mathcal{H}_0$ be the trial functional space. Following the standard rules of the calculus of variations, the variational-equivalent problem to the one stated in Eqn. (5) is

$$\Phi(\{\beta\},\{\gamma\}) = \max_{\{h_0\} \in \mathcal{H}_0} (k_B \{\beta\}^T \{\langle h - h_0 \rangle_0\} - k_b \log \Xi_0) =$$
$$- \min_{\{h_0\} \in \mathcal{H}_0} \mathcal{F}[\{h_0\},\{\beta\},\{\gamma\}].$$

(6)

Related with the trial energy h_0, we have the *trial phase space* z_0, and the difference between the physical phase space and the trial one is defined as $z' = z - z_0$. By appealing to the arbitrariness of h_0, we will adopt a convenient gaussian structure. Taking this into account, h_0 has the following structure

$$\{h_0\} = \tfrac{1}{2}\{z'\}^T Q \{z'\} - k_B T \{\gamma_0\}^T \{n\} =$$
$$\begin{cases} \frac{k_B T}{2\sigma_i^2}|q_i - q_{0i}|^2 + \frac{1}{2m_i}|p_i - p_{0i}|^2, & \text{if } i \in I_{Mg} \\ \frac{k_B T}{2\sigma_i^2}|q_i - q_{0i}|^2 + \frac{1}{2m_i}|p_i - p_{0i}|^2 - k_B T \gamma_{0i} n_i, & \text{if } i \in I_H. \end{cases}$$

(7)

Where a uniform temperature T has been considered seeking simplicity in further developments. After a careful inspection of Eqn. (7), it can be shown that q_{0i} and σ_i are the mean and standard deviation of q_i, whereas p_{0i} is the mean of p_i. Finally, γ_{0i} indicates the dependence of chemical potential on H fraction χ_i.

Substituting Eqn. (7) into Eqn. (6), and after straightforward algebraic manipulations, the optimization problem becomes

$$\min_{\{\bar{q}\},\{\bar{\sigma}\},\{\bar{p}\}} \mathcal{L}_0[\{h_0\},\{\gamma\}]$$
$$= k_B \log \Xi_0 + \frac{1}{T}\langle V \rangle_0 + \frac{1}{2}N k_B$$
$$- k_B \left(\sum_{i \in I_{Mg}} \gamma_i + \sum_{i \in I_H} \gamma_i \frac{e^{\bar{\gamma}_i + \gamma_i}}{1 + e^{\bar{\gamma}_i + \gamma_i}} \right),$$

(8)

where $V(\{q\},\{n\})$ denotes a general interatomic potential energy. The corresponding Euler-Lagrange equations are

$$\begin{cases} \frac{\partial \mathcal{L}_0}{\partial \bar{q}_i} = \langle \frac{\partial V}{\partial q_i} \rangle_0 = 0, \\ \frac{\partial \mathcal{L}_0}{\partial \bar{\sigma}_i} = \frac{3 k_B}{\bar{\sigma}_i} + \frac{1}{T}\frac{\partial \langle V \rangle_0}{\partial \bar{\sigma}_i} = 0, \\ \frac{\partial \mathcal{L}_0}{\partial \gamma_i} = k_B \frac{e^{\bar{\gamma}_i + \gamma_i}}{(1 + e^{\bar{\gamma}_i + \gamma_i})^2}(1 + e^{\bar{\gamma}_i + \gamma_i} - \gamma_i) = 0. \end{cases}$$

(9)

We may regard the first equation as the *meanfield* condition of quasistatic equilibrium for the mean atomic positions $\{q\}$, the second equation is known as the mean field optimality condition, and the third equation stands for the chemical equilibrium. The presented system of Eqns. (10) is not closed. In order to close the system, *kinetic equations* for the evolution of the atomic molar fraction needs to be appended as in Ref. [18]. Without loss of generality, we begin by noting the mass flow into the site i may be expressed in conservation form as

$$\dot{\chi} = \sum_{j,j \neq i} J_{ij},$$

(10)

where $J_{ij} = -J_{ji}$ is the discrete mass flux array from site j to site i. The conjugate measure of J_{ij} is K_{ij}, which measures the *internal entropy production rate* defined as

$$K_{ij} = k_B(\gamma_i - \gamma_j).$$

(11)

Following Onsager, we postulate kinetics laws of the general form

$$J_{ij} = -\frac{\partial \psi(\{K\})}{\partial K_{ij}},$$

(12)

where ψ is a discrete kinetic potential, to be modeled. In that sense, Eqn. (12) can be regarded as a *discrete Fick law* of diffusion. Following Refs. [10], [19] the mass transport equation takes the form

$$\frac{\partial \chi_i}{\partial t} = - \sum_{j,j \neq i} \frac{\partial \psi(\{K\})}{\partial K_{ij}}$$

$$\frac{\partial \chi_i}{\partial t} = \sum_{\langle i,j \rangle} v_i e^{-\beta E_b} \left(\chi_j(1 - \chi_i) e^{\beta(\mu_j - \mu_i)/2} \right.$$
$$\left. - \chi_i(1 - \chi_j)e^{\beta(\mu_i - \mu_j)/2} \right)$$

(13)

Where the sum runs over all connected neighbors, v is the hoping frequency, and E_b is a barrier energy which

can be calibrated using the macroscopic diffusion coefficient, see Refs. [14], [18].

3. THE MEANFIELD ADP POTENTIAL

For the system MgHx we consider the Angular Dependent Potential (ADP) proposed by Mishin, see Ref.[20], since it is more adequate in description of non-cubic structures. This aspect is crucial if we want to describe the phase transition of Mg properly. This process occurs during the formation of the hydride MgH$_2$, see Ref.[15]. On top of that, to accommodate the ADP to the present approach we will be interested in the macroscopic value or expected value of the potential V. Therefore, following the *max-ent* formalism, the thermalized value of V is given by the following expression

$$\langle V \rangle_0 = \langle V^\phi \rangle_0 + \langle V^F \rangle_0 + \langle V^\mu \rangle_0 + \langle V^\lambda \rangle_0$$

(14)

The term $\langle V^\phi \rangle_0$ represents pair-interactions between atomic sites *via* the pair potential $\phi_{ij}(r_{ij})$

$$
\begin{aligned}
\langle V^\phi \rangle_0 = & \frac{1}{2} \sum_{i \in I_{Mg}, j \in I_{Mg}, j \neq i} \langle \phi_{ij}(r_{ij}) \rangle_0 \\
& + \frac{1}{2} \sum_{i \in I_{Mg}, j \in I_H, j \neq i} \chi_j \langle \phi_{ij}(r_{ij}) \rangle_0 \\
& + \frac{1}{2} \sum_{i \in I_H, j \in I_{Mg}, j \neq i} \chi_i \langle \phi_{ij}(r_{ij}) \rangle_0 \\
& + \frac{1}{2} \sum_{i \in I_H, j \in I_H, j \neq i} \chi_i \chi_j \langle \phi_{ij}(r_{ij}) \rangle_0,
\end{aligned}
$$

(15)

where the summation is over all j-th neighbors of i-th atom within a cut-off distance. The second term, $\langle V^F \rangle_0$, is the embedding energy that is a function of the total electron density and represents many-body interactions between atoms

$$\langle V^F \rangle_0 = \frac{1}{2} \sum_{i \in I_{Mg}} F(\bar{\rho}_i) + \frac{1}{2} \sum_{i \in I_H} \chi_i F(\bar{\rho}_i)$$

(16)

The function $F(\bar{\rho}_i)$ is the embedding energy of atom i in the host electron density $\bar{\rho}_i$ induced at site i by all other atoms of the system. The host electron density is given by

$$\bar{\rho}_i = \sum_{j, j \neq i, j \in I_{Mg}} \rho_j(|r_{ij}|) + \sum_{j, j \neq i, j \in I_H} n_j \rho_j(|r_{ij}|)$$

(17)

Where ρ_j is the electron density function assigned to an atom j.

This two first terms in Eqn. (14), give the principal contribution to the system energy. Additionally, the two remaining terms, $\langle V^\mu \rangle_0$ and $\langle V^\lambda \rangle_0$, introduce non-central interactions through the dipole vectors and quadrupole tensors. They are intended to reflect deviations of local environment from the cubic symmetry. The contribution of the dipole term is given by the scalar product of the measure of the dipole distortion, μ_i, at the local environment of atom i

$$\mu_i = \sum_{j, j \neq i} n_i \, n_j \, u(|r_{ij}|) \, r_{ij}$$

(18)

After some algebraic manipulations and taking the thermal average the contribution of the dipole term to the thermalized potential is

$$
\begin{aligned}
\langle V^\mu \rangle_0 &= \frac{1}{2} \sum_i \langle \mu_i \cdot \mu_i \rangle_0 \\
&= \frac{1}{2} \sum_i \sum_{\langle j, j^* \rangle, \, j, j^* \neq i} u(|r_{ij}|) \, u(|r_{ij^*}|) \, (r_{ij} \cdot r_{ij^*})
\end{aligned}
$$

(19)

The contribution of the quadrupole term is given by the deviatoric part of the quadrupole term λ_i

$$\langle V^\lambda \rangle_0 = \frac{1}{2} \sum_i \langle \lambda_i : \lambda_i \rangle_0 - \frac{1}{6} \sum_i \langle tr(\lambda_i)^2 \rangle_0$$

(20)

where λ_i is

$$\lambda_i = \sum_{j, j \neq i} n_i \, n_j \, w(|r_{ij}|) \, r_{ij} \otimes r_{ij}$$

(21)

As in the Modified Embedded-Atom Method (MEAM) and Electric Dipole Moments (EDM) methods, the role of the angular terms, $\langle V^\mu \rangle_0$ and $\langle V^\lambda \rangle_0$ is to penalize the total energy for deviations of the atomic environments from cubic symmetry. While these terms vanish in a perfect cubic structure such as fcc or bcc regardless of its volume due to the properties of the scalar product, they take non-zero values under non-hydrostatic strains and thus affect the elastic constants of both cubic and non-cubic crystals. These terms are especially important in non-centrosymmetric structures hpc likewise pure Magnesium. A final remark on this section is, thermal averages, $\langle \cdot \rangle_0$, required for the evaluation of the potential can be calculated by recurse to third-order Hermitian quadrature [21], however, the higher order terms which arise due to the presence of the dipole and quadrupole contribution may affect the accuracy of the early mentioned integration rule, this aspect will be covered in future research.

4. SUMMARY AND CONCLUDING REMARKS

We have introduced an ADP-based DMD model which is more appropriate to reproduce the phase transition of Magnesium during hydrogenation than conventional potentials. The main advantage of this approach is the ability to consider phase transitions in the Magnesium lattice structure during the hydrogen diffusion process.

Therefore, the large time window and atomistic resolution of DMD renders it an excellent tool for studding hydride phase-transformation within Mg nanoparticles, which operates on time scales of seconds to minutes.

As already mentioned, the narrow aim of this paper focus on the proposal of a formulation rather. Whereas aspects such as the rigorous description of the model, its numerical resolution and ability predict macroscopic mechanical properties of Mg and MgH$_x$ such as thermal expansion, bulk and poisson moduli will be assessed in a future publication.

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