New interatomic potential for simulation of pure magnesium and magnesium hydrides

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ABSTRACT

We develop an interatomic potential intended for the study of Mg-H system using atomistic methods. The reported potential has an angular-dependent form and can be used for simulation of pure magnesium, as well as for consideration of binary cases including Mg and H. Summary of the performed tests on elastic, thermophysical and diffusional properties proves that the potential has a wide range of applicability. For example, it can be used to model phase transitions existing in pure magnesium (liquid ↔ hcp and bcc ↔ hcp). We also show how the model represents energies of different point defects and stacking faults in Mg. The primary purpose of the potential is the simulation of hydrogen behavior in magnesium. Here we show examples of the hydrogen diffusion and clusterization in hcp magnesium. Also, it is shown that the proposed potential reproduces stable structures for some of the existing magnesium hydrides: α-MgH$_2$ (P4$_2$/mnm) and γ-MgH$_2$ (Pbcn).

1. Introduction

The use of hydrogen as an energy source opens up a promising way of energy obtaining, which is alternative to the existing fossil fuel-based energetics [1,2]. Along with the possibility of environmentally friendly methods of obtaining power, hydrogen can provide the lightest fuel that is the richest in energy per unit mass. However, to achieve this goal, it is necessary to solve the technological challenge of the optimal hydrogen storage. One of the most promising ways here is to use the metal hydrides, which incorporate hydrogen into their crystal structure [3]. Within such approach, hydrides hold hydrogen at low temperatures and high pressures and discharge it when needed by raising their temperature or decreasing the external pressure [4]. Practically, much attention is paid here to magnesium and aluminum hydrides.

According to the recent considerations [4], magnesium might give an effective practical option for hydrogen storage: it allows to perform reversible hydriding and combines high hydrogen capacity with a rather low material coast. So, there is an interest in the experimental and theoretical study of the properties of the magnesium-hydrogen system. However, the slow hydriding/dehydriding kinetics and relatively high dissociation temperature (>600 K) currently hinder the practical applications of this material [5]. To overcome these difficulties, new techniques of altering the hydride characteristics are under

development; they can include mechanical processing, doping, alloying or altering the hydride structure [6]. For all these methods information about the behavior of magnesium and its hydrides under different pressure-temperature conditions is highly required. In such case, an appropriate model could be useful to estimate the characteristics, including the formation (or decomposition) of the hydride, and hydrogen diffusion in a metal. The prominent way to get theoretical predictions is the use of *ab initio* methods such as density-functional theory (DFT) calculations. Such methods are widely adopted for investigation of the metals, as well as for the description of the defects and impurities behavior [7], including that in magnesium hydrides. For example, Du et al. [8] used quantum-mechanical calculations to analyze the desorption of H$_2$ from different surfaces of the rutile-type structure of MgH$_2$. Maark et al. [9] applied DFT calculations to estimate the impact of Al- and Si-dopants on the hydrogen adsorption energy and band structure of different magnesium hydrides. A question regarding the stability of different hydride structures at various pressures and temperatures was also considered theoretically in work [6].

The computational limitations of *ab initio* methods prevent their use to study of the larger scale phenomena. For example, such calculations are not appropriate for estimates of the diffusion coefficients in solid phases, and it provides no opportunity to study the interaction of hydrogen the with the extended defects (i.e., grain boundaries or

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dislocations). The optimal way to consider such material science problems is the molecular dynamics (MD) simulation based on the use of interatomic potential. However, to our knowledge, no potential for Mg-H system have been reported. At the same time, there is a bunch of potentials aimed at simulation of pure magnesium [10–15]. In this work, we report a new interatomic potential developed for the study of the binary Mg-H system. In Section 2 we give details of the potential development technique. Section 3 contains a summary of the verification tests illustrating representation of pure magnesium properties, including questions of phase stability. Section 4 is devoted to simulation of the hydrogen behavior in magnesium. In Section 5 we discuss results obtained from the study of magnesium hydrides MgH_2.

2. Development of an interatomic potential for Mg-H system

In this work, we develop an interatomic potential for description of the binary Mg-H system. For this purpose, we adopted a concept of the Angular-Dependent Potential (ADP). This model was offered in [16] as an extension of the embedded-atom method (EAM) that originally gave a way to formalize description of the many-body interactions in metals [17]. In the ADP, the total potential energy U for a binary system is given by the following equation:

$$U = \sum_{i>j} \varphi_{\alpha\beta}(r_{ij}) + \sum_i F_\alpha(\overline{\rho}_i) + \frac{1}{2}\sum_{i,k}(\mu_i^k)^2 + \frac{1}{2}\sum_{i,k,l}(\lambda_i^{kl})^2 - \frac{1}{6}\sum_i \nu_i^2,$$ (1)

where the notations are interpreted as follows:

$$\overline{\rho}_i = \sum_{j\neq i}\rho_\beta(r_{ij}), \quad \mu_i^k = \sum_{j\neq i}u_{\alpha\beta}(r_{ij})r_{ij}^k,$$

$$\lambda_i^{kl} = \sum_{j\neq i}w_{\alpha\beta}(r_{ij})r_{ij}^k r_{ij}^l, \quad \nu_i = \sum_k \lambda_i^{kk}.$$ (2)

Here indices i and j enumerate atoms, while superscripts k, l = 1, 2, 3 refer to the Cartesian components of vectors and tensors. Indices α and β denote the element types of atoms. The first term in Eq. (1) represents pair interactions between atoms *via* a pair potential φ. The summation is performed over all j-th neighbors of i-th atom (within the cut-off distance r_{cut}, which we set to 6.3 Å). The second term F in Eq. (1) is the embedding energy that is a function of the total electron density $\overline{\rho}$. The first two terms in Eq. (1) are similar to those introduced within the classical EAM model. Additional terms (μ and λ) introduce non-central interactions through the dipole vectors and quadrupole tensors. Due to this functional improvement, the ADP is supposed to be more accurate in description of non-cubic structures, compared with EAM potential [18].

To determine the potential functions included in the Eq. (1), we applied the force-matching method [19]. It gives a way to construct physically justified interatomic potentials from the fitting database containing no experimental data. The idea is to adjust the interatomic potential functions (performed as a set of cubic splines) to optimally reproduce per-atom forces (together with total energies and stresses) computed at the *ab initio* level for a fine-tuned set of reference structures (i.e., configurations). In this work, the potential functions were optimized using realization of the force-matching method implemented in the *Potfit* code [20,21].

The fitting procedure is directed by minimization of the target function Z given by the following sum:

$$Z = Z_f + Z_C,$$ (3)

$$Z_f = \sum_{i=1}^{N_f}\sum_{\alpha=x,y,z}W_i(f_{i\alpha}^{ADP}-f_{i\alpha}^{DFT})^2,$$ (4)

$$Z_C = \sum_{j=1}^{7N_C}W_j(A_j^{ADP}-A_j^{DFT})^2.$$ (5)

Table 1

Description of the reference structures used for fitting of the potential. Here N_c is the number of structures of the given type, n_{at} is the number of atoms in a single structure, W is the attributed weight. The minimum and maximum values of temperature T (in K) and atomic volume V (in Å^3) for one group of configurations are also shown. The volume is given per atom for the one-component structures and per chemical unit (i.e., MgH_2) for the hydrides.

Structure	N_c	n_{at}	W	T_{min}–T_{max}	V_{min}–V_{max}
Configurations with attributed forces					
hcp Mg	21	180	1–6	300–900	14.3–22.8
bcc Mg	5	128	1	300–600	12.0–22.3
liquid Mg	9	128	1	1000–2800	14.9–21.4
Mg + H	3	108 + H[a]	1	400–800	17.5–18.0
α-MgH$_2$	4	216	1	400–800	29.4–31.0
γ-MgH$_2$	1	216	1	500	29.6
pure H	2	64	1	1000	20.0–25.0
Configurations without attributed forces					
hcp Mg	1	96	15	0	22.80
fcc Mg	1	108	35	0	22.90
hcp Mg	3	96	1	0	22.85

[a] In this type of structures hydrogen was placed in the interstitial positions within the hcp lattice of magnesium. The number of H atoms in the given structure was equal to 8, 12 or 17.

Here Z_f and Z_C denote two separate parts of the target function for per-atom forces f and integral characteristics A (include energy and components of the stress tensor). Here N_f is the total number of atoms for which the forces are taken into account during the minimization. N_C is the total number of configurations. For each configuration, we have one value of the energy and six components of the stress tensor. W_i and W_j are the weights attributed to different values taking part in the potential fitting. Index "DFT" denotes the reference value calculated using the DFT code VASP [22]; "ADP" denotes the value computed with the fitted potential.

2.1. Description of the reference structures

Each of the reference structures (or so-called *configurations*) contains about 100 atoms in a simulation box with periodic boundary conditions (PBC). Detailed list of the configurations attributed with their description is given in Table 1. All these configurations were obtained from classical atomistic simulations (MD or static) carried out at different temperatures T and volumes V. In this case, the value of T correlates with averaged displacements of atoms from the lattice site positions. To simulate the structures examples at the initial step of the work, we applied the trial interatomic potentials: for Mg from [12] and for Ti-H from [7]. The latter was used to get the first assumption for binary structures existing in the Mg-H system. All MD and static calculations reported here and below were performed with the LAMMPS [23] code.

The configurations listed in Table 1 are divided into two groups. The first group of structures was obtained from MD, and all forces, energies, and stresses for them were included in the fitting process. Here almost all configurations were fitted with the default weights (W_i and W_j equal to 1. The only exception was made for the six structures illustrating uniaxially deformed hcp Mg. The latter were attributed by $W_i = W_j = 6$ to get better representation of the elastic properties. The second group of structures includes that obtained from static calculations performed at zero pressure and temperature. Here we have structures of undisturbed fcc and hcp lattices (which help to fit the energy ratio), and a set of three structures containing information regarding stacking faults. The weights W_j for these structures are also shown in Table 1. In total, for construction of the potential, we use 55 configurations. The Table 1 contains information about 50 of them, and the rest five were so-called normalizing configurations containing the low-density structures of Mg and H necessary to correctly describe the zero interaction energies at large interatomic distances.