Molecular Dynamics Simulations on Hydrogen Diffusion in Copper Using Machine-Learned Interatomic Potential

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1. Introduction

In fusion reactors, plasma-facing materials (PFMs) are exposed to intense heat, neutron, and plasma (hydrogen isotope and helium) flux. The divertor, in particular, faces the most extreme operating conditions [1]. The tungsten and copper (W/Cu) monoblock design, which applies tungsten with high thermal resistance and copper with a high thermal conductivity as a heat sink, is considered a promising divertor design for many fusion reactor programs, including the ITER project [2].

Hydrogen-metal interaction is one of the various interactions that materials encounter in fusion environments. Copper and its alloys behind the tungsten armor are not directly exposed to the fusion plasma; however, hydrogen can still be introduced to the copper layer by diffusion from a W surface or due to cracks on the surface. Implanted hydrogen may degrade mechanical integrity by embrittlement, blistering, and volumetric expansion, which will limit the performance and lifetime of W/Cu monoblocks.

Molecular dynamics (MD) simulations can provide a theoretical approach to studying hydrogen behaviors and effects in metals. However, the accuracy of MD simulation results is highly dependent on the quality of the interatomic potential model applied. Although several Cu-H interatomic potentials, such as the embedded atom method (EAM) potential [3-5] and bond-order potential (BOP) [6], have been developed, their accuracy is limited compared to first-principles calculations.

In this research, we constructed a machine-learned potential model in the form of the moment tensor potential (MTP) [7] to assess the diffusivity of hydrogen isotopes (HIs) in bulk copper using MD. The MTP was trained using energy, force, and stress data derived from density functional theory (DFT) calculations of pure copper and copper-hydrogen systems to achieve comparable accuracy to DFT. The quality of MTP was validated by comparing calculated physical properties with experimental and DFT-calculated results. This research serves as a first step toward comprehensive investigations into hydrogen behaviors and effects in W/Cu monoblocks.

2. Methods

This section describes the computational approach we applied to construct an MTP using the Machine Learning Interatomic Potential (MLIP) package [7] and to compute the diffusion coefficients of HIs in copper using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code [8].

2.1 Construction of MTP

A machine learning potential is generally trained to reproduce energy, force, and stress data derived from DFT calculations. Among the reported machine learning interatomic potential models, we selected MTP. In the MTP, the potential energy of each atom is evaluated by a linear combination of the basis functions representing the local atomic environment within a cutoff distance. Each basis function consists of a radial part expressed as Chebyshev polynomials and an angular part expressed as moment tensors with outer products of neighboring atomic positions. The size of the basis functions is controlled by the hyperparameter called *level*. Generally, an MTP with a higher level consists of complex basis functions and thus reproduces DFT data more precisely with the trade-off of increased computational time.

For K configurations prepared as the training set, the linear combination coefficients of the basis functions are optimized to minimize the loss function given as equation (1)

$$(1)\quad \sum_{i=1}^{K}\Big[\frac{w_e}{(N_i)^2}\left(E^{MTP}(cfg_i)-E^{DFT}(cfg_i)\right)^2 + \frac{w_f}{N_i}\left|f^{MTP}(cfg_i)-f^{DFT}(cfg_i)\right|^2 + \frac{w_e}{(N_i)^2}\left|\sigma^{MTP}(cfg_i)-\sigma^{DFT}(cfg_i)\right|^2\Big],$$

where N_i is the number of atoms in the i-th configuration cfg_i, and w_e, w_f, and w_s are the weights for energy, force, and stress, respectively. The hyperparameters were set as follows: the minimum and maximum cutoff distances of 0 Å and 6 Å, respectively, level of 16, and w_e, w_f, and w_s of 1, 0.1, and 0.01, respectively.

DFT calculations were performed to obtain energy, force, and stress data of each configuration as training set. The Vienna Ab initio Simulation Package (VASP) code [9] was used for DFT calculations. The PBE functionals of generalized gradient approximations (GGA) [9] were adopted to evaluate the exchange-correlation energy. The effect of core electrons on valence electrons was treated using the projector augmented wave (PAW) method with *PAW_PBE Cu 22Jun2005* and *PAW_PBE H 15Jun2001* data files contained in the VASP package.

The automatic scheme implemented in VASP was used with a length parameter of 50 to define the k-point sampling grid for the band energy calculations, and the cutoff energy of the plane wave basis was set to 700 eV.

The training set was prepared by combining supervised and active learning schemes. The details of the prepared training set will be explained in the presentation.

2.2 Validation of MTP

The performance of the constructed MTP model was tested with the LAMMPS code for (1) the potential energy of randomly selected configurations, (2) several physical properties of Cu, and (3) the solution energy of H at interstitial sites of Cu.

For (1), 120 configurations were sampled as a validation set at temperatures of 300, 600, 900, and 1200 K for $Cu_{32}H_1$ under NPT ensembles. The energy calculated by the MTP for each configuration was compared to the DFT calculation.

For (2), the lattice constant and elastic constants at 0 K were calculated from the relation between stress and applied stain. Lattice constants at finite temperatures were calculated by averaging lattice constants in NPT ensembles.

For (3), the solution energy was calculated for $Cu_{32}H_1$ with hydrogen at a tetrahedral or octahedral site.

2.3 MD simulation for diffusion coefficients

The diffusion coefficients of HIs in copper were obtained by MD from 500 K to 1200 K, which includes the operating temperature of the Cu region in ITER-like W/Cu monoblocks [10]. The equilibrium volume at each temperature was obtained by averaging the volume of a Cu_{256} supercell for a production run of 0.1 ns after an equilibration run of 0.1 ns in an NPT ensemble. Subsequently, the mean square displacement (MSD) [11] of the hydrogen atom in a $Cu_{256}H_1$ supercell was evaluated in an NVT ensemble with the pre-determined equilibrium volume of Cu_{256}. After an equilibration run of 50 ps, the MSD-time relation was measured for 2 ns. Finally, the diffusion coefficient was determined according to the Einstein relation by linearly fitting relation between MSD and simulation time.

3. Results and Discussions

3.1 Validation of constructed MTP

Firstly, the fitting quality of MTP was assessed using the root mean square error (RMSE) of energy, force, and stress with respect to the DFT data in the training set. These errors were 2.191 meV/atom for energy, 0.404 eV/Å for force, and 0.202 GPa for stress. Figure 1 illustrates the comparison between system energies calculated by the MTP and DFT for the validation set, demonstrating a reasonable match with a mean absolute error of 0.3 meV/atom and an RMSE of 0.4 meV/atom.

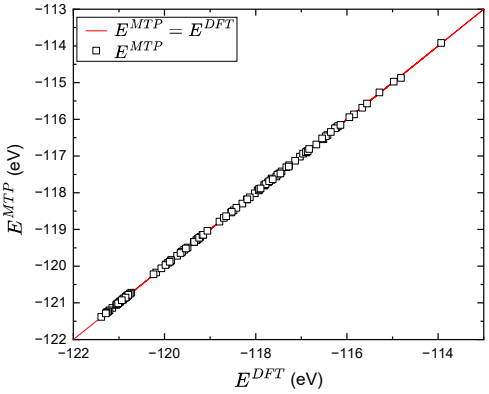

Fig. 1. Calculated system energies of the validation set composed of randomly selected 120 $Cu_{32}H_1$ configurations by MTP and DFT.

Subsequently, several material properties of fcc-Cu were calculated by MD using LAMMPS, such as (1) lattice constant, (2) elastic constants, (3) linear thermal expansion coefficient, and (4) solution energy of hydrogen in interstitial sites. The calculation results are compared with DFT and experimental data in Table 1. Table I confirms that the developed MTP can reasonably reproduce the lattice properties of fcc-Cu as well as hydrogen-related properties.

Table I : Comparison of lattice constant at 0 K (a_0), 300 K (a_{300}), and 1200 K (a_{300}), cohesive energy of pure fcc-Cu ($E_{coh\_fcc\text{-}Cu}$), elastic constants (C_{11}, C_{12}, C_{44}), linear thermal expansion coefficient at room temperature (α_{300K}) and near melting temperature (α_{1200K}), and hydrogen solution energy at octahedral site ($E_{sol\_oct\text{-}H}$) and tetrahedral site ($E_{sol\_tet\text{-}H}$) with DFT and experiment [12].

	MTP	Reference
a_0 (Å)	3.632	3.633 [DFT]
C11(GPa)	174.2	178.7 [DFT]
C12(GPa)	120.0	117.2 [DFT]
C44(GPa)	76.6	84.7 [DFT]
a_{300} (Å)	3.652	3.615 [12]
a_{1200} (Å)	3.727	3.681 [12]
α_{300K} (10^{-6} K^{-1})	19.61	16.76 [12]
α_{1200K} (10^{-6} K^{-1})	16.28	23.08 [12]
$E_{coh\_fcc\text{-}Cu}$(eV)	-3.653	-3.728 [DFT]
$E_{sol\_oct\text{-}H}$ (eV)	0.419	0.431 [DFT]
$E_{sol\_tet\text{-}H}$ (eV)	0.620	0.638 [DFT]

3.2 Hydrogen diffusion coefficients in copper

Figure 2 presents the evaluated diffusion coefficients of hydrogen isotopes in fcc-Cu by developed MTP alongside previous experimental studies. These hydrogen calculations were performed at 500, 600, 800, 1000, and 1200K, while deuterium and tritium calculations were done only at 800 and 1200 K. The standard error of the mean in the calculated diffusion coefficient was less than 12% each. By Arrhenius plot, we derived a pre-exponential factor (D_0) of 6.47×10^{-7} m^2s^{-1} and an activation energy (E_b) of 0.318 eV for hydrogen diffusion. Although some overestimation tendency was observed, fair agreement with experimental data was confirmed. The isotope effects, assessed with diffusion coefficient ratios for deuterium and tritium relative to hydrogen, were 1.22±0.26 and 1.43±0.26 at 800 K and 1.19±0.17 and 1.41±0.18 at 1200 K, respectively. These results were in accordance with prior experimental studies [13-16]. While the effect of mass difference was evident, it was less significant than the classical theory, which is expressed as inversely proportional to the square root of the mass.

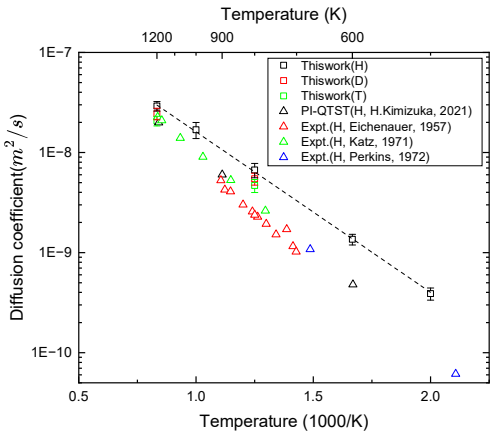

Fig. 2. Diffusion coefficients of hydrogen isotopes determined by MD simulations using the constructed MTP (represented as squares) compared to previous experimental and theoretical studies [12-16] (represented as triangles). The broken line denotes the Arrhenius equation obtained by linear regression with hydrogen diffusion coefficients calculated with the MTP.

4. Conclusions

We developed the machine-learning MTP to compute diffusion coefficients of hydrogen isotopes in fcc-Cu. The calculated material properties and hydrogen solution energy of fcc-Cu agreed well with DFT and experimental values. The evaluated hydrogen diffusivity also showed fair consistency with experiments, although some overestimation tendency was observed. In future studies, we plan to (1) improve the accuracy of the current MTP by refining the training set and (2) extend it to a W-Cu-H potential model to simulate HIs behaviors in W/Cu monoblocks for ITER and other fusion reactors.

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