

# Development of Machine Learning Interatomic Potential to Describe Hydrogen Behavior in Alpha Zirconium

Seong-been Lee, Takuji Oda\*

Department of Nuclear Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826

\*Corresponding author: oda@snu.ac.kr

**\*Keywords: Zirconium; Hydrogen diffusion; Machine-learning potential; Atomistic simulations**

## 1. Introduction

Zirconium (Zr) alloys are widely used as cladding materials in nuclear reactors, primarily due to their favorable thermodynamical, mechanical, and nuclear physics properties. However, the ductility of the cladding material significantly diminishes when hydrogen accumulates beyond its solubility limit, forming hydrides. Due to the complex effects of temperature, stress field, and microstructures on the behaviors of hydrogen solutes and the stability of hydride phases [1], our comprehension remains limited despite numerous experimental studies.

Molecular dynamics (MD) holds promise as a methodology to investigate zirconium-hydrogen interaction on an atomic scale. To attain reliable simulation results, an accurate interatomic potential model is imperative. However, presently available potential models fall short of effectively capturing the behavior of hydrogen solutes and the formation dynamics of hydrides.

Machine learning interatomic potential (MLIP) has recently attracted much attention due to its excellent accuracy. Therefore, in this study, as a first step to achieve a potential model that accurately describes the Zr-H system, we developed an MLIP to simulate solute hydrogen behaviors in alpha Zr. The validity of the constructed potential model was verified through comparison with the results of experiments and first-principles calculations.

## 2. Methods

### 2.1 First-principles calculation

MLIP is constructed using first-principles calculation results as the training data. In this study, to generate the training data by density functional theory (DFT) calculations, the Vienna ab initio simulation package (VASP), which is a plane wave DFT code, was used. The calculations were performed within the generalized gradient approximation (GGA), and the exchange-correlation energy was described by the Perdew-Burke-Ernzerhof (PBE) functionals. The plane wave basis set with an energy cutoff of 500 eV was applied to expand the electron wavefunction of valence electrons. Twelve electrons were dealt with as valence electrons ( $4s^24p^65s^24d^2$ ) for Zr and one electron for H. The band

energy sampling of the Brillouin zone was performed with a  $\Gamma$ -point centered k-point mesh generated using the automatic k-point mesh scheme implemented in VASP with a length parameter of 50.

### 2.2 Moment Tensor Potentials (MTP)

MTP belongs to the class of machine-learning potentials and can be trained using the MLIP package [2]. The basis function of MTP is composed of radial and angular functions. In the radial functions, the minimum and maximum cutoff distances were set to 0.0 Å and 6.0 Å, respectively. In the domain of angular functions, the number of angular basis functions is controlled by a parameter called "level". Specifically, the level parameter determines how many basis functions are incorporated into the MTP model. The higher the level, the more basis functions are included, which increases computational cost and accuracy. Therefore, it is important to decide the level best to balance the tradeoff between computational accuracy and computational cost when constructing an MTP. In order to find such a compromise, we tested five types of levels: 12, 14, 16, 18, and 20. In addition, since a non-linear iterative methodology is used in constructing MTPs, where the initial parameters have a significant impact, five different initial parameters were prepared for each level, and the best one was selected.

## 3. Result & Discussion

### 3.1 Hyperparameter optimization

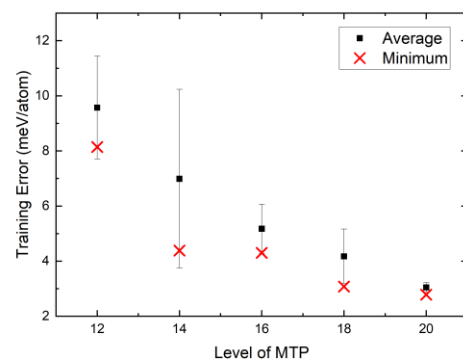


Figure 1. Average and minimum values of training RMSE as a function of MTP level.

**Figure 1** shows the average value and standard deviation in the root mean square error (RMSE) of energy fitting as a function of MTP level. The smallest RMSE among the RMSEs of five MTPs constructed from different initial parameters was also shown at each level. It can be seen that starting at level 16, the average training RMSE decreases to around 5 meV/atom. Therefore, in validation tests, we exclusively employed MTPs with levels of 16 or higher.

### 3.2 Mechanical properties of Alpha Zr

Table 1. Mechanical properties of alpha Zr.

	Lev 16	Lev 20	DFT	Exp.[3]
a (Å)	3.231	3.232	3.232	3.232
c (Å)	5.167	5.169	5.169	5.146
c/a	1.599	1.599	1.599	1.593
B (GPa)	93.04	97.98	91.93	92±3
C11 (GPa)	126.76	126.59	142.19	144
C33 (GPa)	105.68	179.54	167.74	166
C44 (GPa)	15.93	25.67	37.7	33.4
C12 (GPa)	90.55	77.01	66.79	74
C13 (GPa)	74.26	73.76	64.97	67

**Table 1** compares the mechanical properties of alpha Zr obtained by MTP and DFT calculations with experimental values. For the lattice constants calculated by MTP, a good agreement with the DFT calculations and the experimental values is confirmed. For the elastic constants, MTP with level 16 shows some error compared to the reference data, but the error becomes acceptably small with level 20. These results show that the constructed MTP can effectively reproduce the basic mechanical properties of alpha Zr.

### 3.3 Formation of a H interstitial in alpha Zr

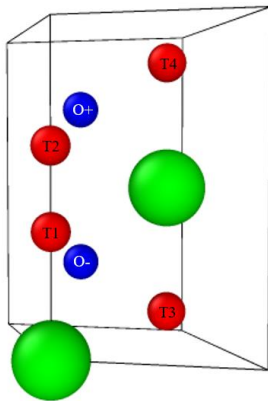


Figure 2. Interstitial sites in an HCP lattice. The green color indicates Zr atom, and the red and blue colors represent tetrahedral and octahedral sites for H atom, respectively.

Table 2. Hydrogen solution energy at tetrahedral and octahedral sites. Ref. [4] is a previous DFT study.

	Lev 16	Lev 20	Ref. [4]	Exp [5]
$E_t$	-0.547	-0.579	-0.520	-0.66
$E_o$	-0.518	-0.491	-0.440	-
$\Delta E$	0.029	0.088	0.080	-

**Figure 2** visualizes the sites where hydrogen can exist inside an HCP unit cell. **Table 2** shows the solution energy of hydrogen at these sites, demonstrating that MTPs fairly reproduce the solution energy, including the energy difference between the two sites.

### 3.4 Hydrogen diffusion in Alpha Zr

Table 3. Activation energy of hydrogen migration in eV unit.

Path	DFT	Lev16	Lev20	Ref. [6]
T1-T2	0.129	0.149	0.161	0.129
T1-T3	0.809	0.873	0.885	-
T-O	0.399	0.347	0.418	0.406
O-T	0.335	0.316	0.328	0.346
O-O	0.39	0.45	0.389	0.398

The activation energy of hydrogen migration was calculated for five different paths, as summarized in **Table 3**. Due to the lack of experimental values for the activation energy of each migration path, DFT calculations from other studies were used as reference data in **Table 3**. In comparison to the reference and present DFT data, the errors in MTP are up to approximately 20%.

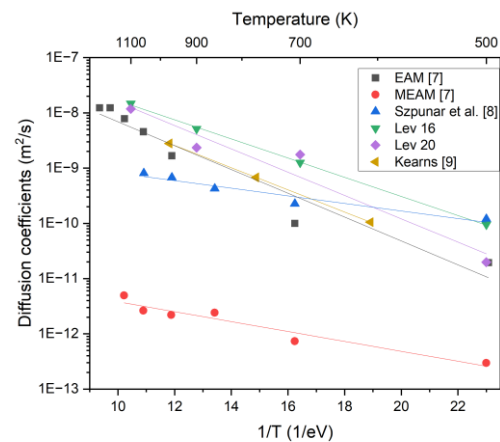


Figure 3. H diffusion coefficients in alpha Zr determined by MD simulations as a function of reciprocal temperature. The results are compared with

other computational study [7] and experimental data [8][9].

Diffusion coefficients were calculated for one H in a 6×6×4 alpha Zr supercell from the relation between the mean square displacement (MSD) and time. The time-MSD relation was obtained over 100 ps, and at least 40 samples were collected for each temperature for averaging.

As **Figure 3** illustrates, the H diffusion coefficient calculated by the MTP models was in good agreement with the experiment. In particular, compared to the diffusion coefficient calculated by Siripurapu et al. using a modified embedded atom method (MEAM) potential, the MTP models have significantly improved values.

Table 4. Calculated activation energy by Arrhenius plot.

Method	Activation Energy (kJ/mol)
MTP - Level 16	38.07
MTP - Level 20	46.44
Kearns [9]	45.31
Siripurapu (EAM) [7]	47.28

As shown in **Table 4**, the MTP model with level 20 shows a good agreement with the experimental data [8]. Compared to the migration energy for each elemental path shown in **Table 3**, the rate-determining step for H migration is considered to be the jump over the T-O path. The relatively small activation energy for the MTP model with level 16 in **Table 4** is consistent with the smaller migration barrier on the T-O path.

#### 4. Conclusion

In this study, we developed the machine-learning interatomic potential to simulate H behaviors in alpha Zr and validated it in terms of several properties of alpha Zr. The hydrogen diffusion coefficient calculated by this MTP model was in good agreement with experimental results compared to other existing potentials. We plan to extend this potential model to describe various zirconium hydrides and then study hydride precipitation and reorientation phenomena on an atomic scale by MD simulations in the future.

#### REFERENCES

- [1] A. T. Motta *et al.*, “Hydrogen in zirconium alloys: A review,” *J. Nucl. Mater.*, vol. 518, pp. 440–460, 2019, doi: 10.1016/j.jnucmat.2019.02.042.
- [2] I. S. Novikov, K. Gubaev, E. V Podryabinkin, and A. V Shapeev, “The MLIP package: moment tensor potentials with MPI and active learning,” *Mach. Learn. Sci. Technol.*, vol. 2, no. 2, p. 025002, 2021, doi: 10.1088/2632-2153/abc9fe.
- [3] I. C. Njifon and E. Torres, “A first principles investigation of the hydrogen-strain synergy on the formation and phase transition of hydrides in zirconium,” *Acta Mater.*, vol. 202, pp. 222–231, 2021, doi: 10.1016/j.actamat.2020.10.030.
- [4] Y. Udagawa, M. Yamaguchi, H. Abe, N. Sekimura, and T. Fuketa, “Ab initio study on plane defects in zirconium-hydrogen solid solution and zirconium hydride,” *Acta Mater.*, vol. 58, no. 11, pp. 3927–3938, 2010, doi: 10.1016/j.actamat.2010.03.034.
- [5] Y. Fukai, *The metal-hydrogen system: Basic bulk properties*, Springer Science & Business Media, 2006.
- [6] Y. Zhang, C. Jiang, and X. Bai, “Anisotropic hydrogen diffusion in  $\alpha$ -Zr and Zircaloy predicted by accelerated kinetic Monte Carlo simulations,” *Sci. Rep.*, vol. 7, no. December 2016, pp. 1–13, 2017, doi: 10.1038/srep41033.
- [7] R. K. Siripurapu, B. Szpunar, and J. A. Szpunar, “Molecular Dynamics Study of Hydrogen in  $\alpha$ -Zirconium,” *Int. J. Nucl. Energy*, vol. 2014, pp. 1–6, 2014, doi: 10.1155/2014/912369.
- [8] J. A. Szpunar, W. Qin, H. Li, and N. A. P. Kiran Kumar, “Roles of texture in controlling oxidation, hydrogen ingress and hydride formation in Zr alloys,” *J. Nucl. Mater.*, vol. 427, no. 1–3, pp. 343–349, 2012, doi: 10.1016/j.jnucmat.2012.05.005.
- [9] J. J. Kearns, “Diffusion coefficient of hydrogen in alpha zirconium, Zircaloy-2 and Zircaloy-4,” *J. Nucl. Mater.*, vol. 43, no. 3, pp. 330–338, 1972, doi: 10.1016/0022-3115(72)90065-7.