

INTERATOMIC POTENTIALS IN THE SYSTEMS Pd-H AND Ni-H

G.M. Poletaev^{1*}, M.D. Starostenkov¹, S.V. Dmitriev²

¹Altai State Technical University, Lenin Str. 46, Barnaul, 656038, Russia

²Institute for Metals Superplasticity Problems, Khalturin Str. 39, Ufa, 450001, Russia

*e-mail: gmpoletaev@mail.ru

Abstract. Interatomic potentials are developed to model hydrogen impurities in Pd and Ni. The H-H potentials are constructed taking into account the results of ab initio simulations reported in the literature. The Pd-H and Ni-H potentials are fitted to the experimental data such as the absorption energy, the activation energy of over-barrier diffusion of H in metals, and the H-vacancy binding energy.

1. Introduction

Interaction of hydrogen with metals remains a topic of active studies in the last century [1]. This is because of practical importance of metal-hydrogen systems, they find applications as radiation resistant materials, materials for extra-pure hydrogen filters and isotope fractioning, for accumulation and storage of light gases, for hydrogen transportation, etc. On the other hand, hydrogen can have undesirable effects on metallic materials, for instance, hydrogen embrittlement, corrosion, stress corrosion cracking [2].

Hydrogen atom is the smallest one in the periodic table both in terms of mass and size, it has high solubility and a uniquely high diffusivity in metals [3-5]. Hydrogenation of metals results in their dilatation, but even for large hydrogen concentrations the type of crystal lattice is typically unchanged and thus, the effect of dissolved hydrogen on metals is relatively soft. Metals completely restore their properties after evacuation of hydrogen and this fact opens the possibilities of controllable change of properties of metals by reversible hydrogenation or, in other words, hydrogen treatment of metals [3].

There exist a number of experimental approaches to study the metal-hydrogen systems. However, the information provided by the experimental methods is very often incomplete, the measured properties may have a large dispersion, and interpretation of the experimental results is not obvious because they typically do not uncover the physical nature of many phenomena observed in hydrogenated metals [1, 3]. This is true especially for metals with low hydrogen solubility.

More detailed information can be obtained with the help of theoretical and computational methods such as the first-principle calculations and atomistic modeling based on the use of empirical interatomic potentials. The first-principle simulations are physically more justified but they are highly demanding on computer power and time. Because of this, they cannot be directly applied to the studies of dynamical processes in materials in the nanometer scale related to the evolution of defect structures and thermal fluctuations of atoms. The study of the absorption and diffusion of hydrogen in the crystal lattice and in the vicinity of defects, investigation of the effect of hydrogen on the mobility of defects, as well as prediction of mechanical properties of the hydrogenated materials can be done considering dynamics of relatively large number of atoms. Such molecular dynamics simulations are typically based on semi-empirical interatomic potentials constructed with the help of first-principle calculations taking into account experimental data.

It is well-known that diffusion of hydrogen and helium in metals differs from that of heavier interstitial atoms by exceptionally small diffusion activation energy and by quantum character of diffusion at low temperatures that, for hydrogen in pure metals, remains up to room temperature [2, 3, 6]. At very low temperatures the quantum mechanism of diffusion prevails which occurs through under-barrier quantum tunneling of hydrogen atoms between nearest interstitials. With increase in temperature and in the degree of imperfection of crystal lattice the contribution of under-barrier diffusion sharply decreases and the classical over-barrier diffusion mechanisms start to operate. At temperatures above the room temperature the diffusion of hydrogen is mainly of over-barrier nature [2, 3, 6]. This makes it possible to investigate the diffusion of light interstitial atoms at sufficiently high temperatures in frame of classical molecular dynamics.

By now there exist several types of potentials describing the interaction of atoms in the metal-hydrogen system that differ by the methodology of fitting their parameters to the experimental data and by the form of the potential functions. Most of the potentials developed so far are built on the basis of various first-principle models, and, as a rule, they do not take into account experimental data such as hydrogen diffusion activation energy, binding energy with trapping defects, dilatation, etc. These characteristics are calculated afterwards and very often all of the abovementioned characteristics are not well described simultaneously by one type of interatomic potentials.

In this work the interatomic potentials are developed for the Pd-H and Ni-H systems taking into account the known potentials and the experimental data on the absorption energy, hydrogen diffusion activation energy, binding energy with point defects of crystal lattice, etc. The choice of metals is motivated by the popularity of these fcc metals among researchers of metal-hydrogen systems and by relatively large amount of experimental data reported for them in the literature.

2. H-H interaction in metals

The H₂ molecules adhered to the metal surface dissociate into separate hydrogen atoms due to the weakening of the covalent bond [3]. Inside the crystal lattice and in the defects of crystal lattice hydrogen exists in the atomic form. In the second half of the last century two models of the charge of hydrogen in metals existed, the H⁺ (proton) and the H⁻ (anion) models. In the 80th it was found that the real situation has in fact the features of both models. By means of *ab initio* simulations it has been demonstrated that a proton in metals is screened by the electrons even stronger than in vacuum and it has a charge different from the elementary charge because the hydrogen's electron contributes to the metallic bonding [3].

Semi-empirical potentials describing the interaction of hydrogen atoms embedded into a metal with each other can be divided into two groups. In both cases the parameters of the potentials are fitted to the results of *ab initio* simulations. In the first group, the H-H interactions are calculated in the electron gas of certain density that depends on the type of metal [7-11]. In the work [9] it has been demonstrated that this interaction is considerably weaker than in vacuum. The second group of H-H potentials is constructed based on the consideration of the metallic hydrogen characteristics, typically, the lattice parameter, the sublimation energy, and the bulk modulus, found from the first-principle simulations [12-14]. The potentials of the second group differ considerably from that of the first group by a deeper potential well shifted to the right, meaning a stronger interaction and a larger interatomic distance (Fig. 1). It is worth noting that solid monoatomic metallic hydrogen having fcc lattice exists at temperatures close to 0 K and extremely high pressures, of order of 100 GPa [15]. At smaller pressures solid hydrogen has hcp lattice with H₂ molecules in the lattice points and interaction between them is weaker.

One of the most popular potentials describing H-H interaction in metals is the Daw-Baskes potential constructed by the embedded atom method [7, 8]. In Fig. 1 the repulsive part of the potential is shown by the curve 1. The authors claim that in the derivation of the potential they tried to use minimal number of assumptions and to take into account all the aspects of the electronic structure [7]. At the same time, the cut-off radius of the potential is limited to the first coordination sphere of the fcc lattice. Such a small cut-off radius does not seem realistic and only the repulsive part of the potential can be trusted.

In Fig. 1 the H-H potentials reported in the works [7-14] are reproduced: the repulsive part of the Daw-Baskes potential for H-H bond in Pd and Ni obtained by the embedded atom method (curve 1) [7, 8]; pair potential of the work [10] for the H-H bond in Al (curve 2); H-H potential in Ni used in [11] (curve 3) (according to the authors, for the repulsive part of their potential they used the repulsive part of the Daw-Baskes potential, however, as it can be seen from the figure, they have shifted it to the right for the reason not explained in their work); potential of the work [12] that takes into account only the repulsive force for the H-H interaction in Pd and Ag (curve 4); H-H potential in Al from the work [13] (curve 5); the H-H potential in several hcp metals from the work [14] (curve 6). Potentials 4 to 6 belong to the second group, i.e., they are constructed with the use of the solid hydrogen characteristics. They are shifted to the right in comparison to the potentials of the first group. They also have a deeper potential well, as it has been mentioned.

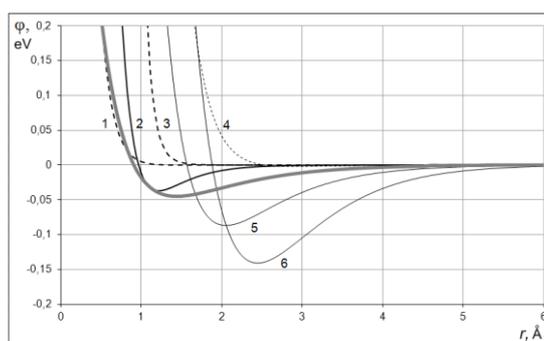


Fig. 1. H-H potentials in metals: 1 – in Pd and Ni [7, 8]; 2 – in Al [10]; 3 – in Ni [11]; 4 – in Pd and Ag [12]; 5 – in Al [13]; 6 – in several hcp metals [14]. Potential developed in the present work is shown by the bold grey line.

The H-H potential shown by the curve 5 in Fig. 1 has been tested in the work [16]. In this work was found that due to the relatively deep potential well of the potential, hydrogen atoms tend to coagulate thus reducing the total energy of the system. The hydrogen absorption energy for the potentials of the second group is rather low and this contradicts to the experimental data. For example, at 70 % hydrogen concentration in Al the average hydrogen absorption energy was found to be -0.8 eV [16], which is eight times smaller than in Pd, for which the solubility of hydrogen, as it is well-known, is exceptionally high. In view of this, in the present work, we were oriented on the potentials of the first group, namely, on the potentials shown by the curves 1 and 2 in Fig. 1.

Parameters of the H-H potential offered in this work take into account the results of first-principle calculations obtained by other authors. In the work [9] it has been shown that the H-H potential is relatively soft and it has minimum at about $r=1.5$ Å. The authors of the works [17] and [18] have found that the binding energy between two hydrogen atoms located in the nearest octahedral holes of iron and tungsten (i.e. at the distances 2.03 Å and 2.22 Å, respectively) are equal to 0.044 eV and 0.02 eV, respectively.

To model the H-H, Pd-H, and Ni-H interactions in this work the Morse interatomic potentials is chosen:

$$\varphi(r_{ij}) = D\beta e^{-\alpha r_{ij}} \left(\beta e^{-\alpha r_{ij}} - 2 \right), \quad (1)$$

where α , β , and D are the potential parameters and r_{ij} is the distance between atoms i and j . Morse potentials, in spite of their simplicity and pairwise nature, are capable of describing many properties of metals and alloys [19, 20]. Morse potentials are often used by researchers to describe interatomic interactions in metal hydrogen systems, e.g., [10, 12-14, 21]. Many-body potentials are more realistic for metals but, taking into account error in some experimental parameters they are fitted to, the choice of the pairwise potentials seems to be justified as an alternative approach. Moreover, because of the small atomic weight of hydrogen, its characteristic vibration frequency is much higher than that of metallic atoms, and one has to use one order of magnitude smaller integration time step in molecular dynamics simulations. The use of pair interatomic potentials softens this problem because they are less time consuming.

The H-H potential offered in the present study is depicted in Fig.1 by the bold grey line.

3. Pd-H and Ni-H interactions

Potentials describing the metal-hydrogen interaction are usually built with the help of the first-principle simulations or/and experimental data, but sometimes they are defined as the average of the H-H and Me-Me potentials (Me meaning metal) [10, 11]. Thus developed potentials, in most cases, do not simultaneously describe with a good accuracy such experimental parameters as hydrogen absorption energy, the activation energy of over-barrier hydrogen diffusion in metal (at normal and higher temperatures), the binding energy of hydrogen with a defect (e.g., with vacancy), the dilatation, etc. One of the main goals of the present study is to construct the interatomic potentials capable of reproducing these experimental parameters.

The Me-Me interactions are described by the Cleri-Rosato many-body potentials constructed in frame of the strong bond approximation. Potential energy of i -th atom is defined as follows

$$U_i = \sum_j A \exp \left(-p \left(\frac{r_{ij}}{r_0} - 1 \right) \right) - \sqrt{\sum_j \xi^2 \exp \left(-2q \left(\frac{r_{ij}}{r_0} - 1 \right) \right)}. \quad (2)$$

Here A , p , q , ξ , and r_0 are parameters, r_{ij} is the distance between i -th and j -th atoms. Parameters of the Cleri-Rosato potentials were taken from the work [22]. These potentials were successfully applied for solving some problems with the use of molecular dynamics [23-25].

Hydrogen absorption energy is the energy required for insertion of a hydrogen atom into metal taking into account the energy needed for the H-H bond breaking to dissociate the H_2 molecule. The absorption energy was calculated from

$$E_{ab} = (U_H - U_0) + \frac{1}{2} E_{dis}, \quad (3)$$

where U_0 is the ideal metal crystal potential energy, U_H is the potential energy of crystal containing a hydrogen atom taking into account the structure relaxation, E_{dis} is the hydrogen molecule dissociation energy ($E_{dis} = 4.485$ eV [1, 3, 9]). To evaluate U_H , a hydrogen atom was introduced into an octahedral hole of a computational cell of fcc Pd or Ni followed by relaxation and then quenching to 0 K.

The binding energy between a hydrogen atom and a vacancy E_{bv} was calculated as the difference between potential energy of the computational cell containing a vacancy and a well separated octahedral hole with a hydrogen atom and potential energy of the computational cell with a hydrogen atom in the vacancy. In both cases the dynamic relaxation of the computational cells was carried out followed by quenching to 0 K.

The migration activation energy of a point defect can be found in molecular dynamics simulations by the static or dynamic method. In the static method the energy barrier is calculated along the trajectory of the point defect. Dynamic method relies on the determination of the diffusion coefficient as the function of temperature $D(T)$ considering one defect in the computational cell (a hydrogen atom in our case). The migration activation energy of hydrogen atom E_m can be found from the dependence $\ln D(T^{-1})$ after estimating the slope $tg\alpha$ as follows

$$E_m = -ktg\alpha = -k \frac{\partial \ln D}{\partial (T^{-1})}, \quad (4)$$

where k is the Boltzman constant and T is temperature.

The dynamical method can be also used to find the pre-exponent multiplier in the corresponding Arrhenius equation. The multiplier is proportional to the defect concentration

$$D = \frac{c}{c'} D' = D'_0 N c \exp\left(-\frac{E^m}{kT}\right), \quad (5)$$

where c is the concentration of the considered defects, c' is the concentration corresponding to one defect in a computational cell, D'_0 is the coefficient found from simulations for one defect in the computational cell, N is the number of atoms in the computational cell. The coefficient D'_0 in the Arrhenius equation (5) can be found as the intersection point of the function $\ln D(T^{-1})$ with the ordinate [23].

In this work the migration activation energy of hydrogen over-barrier diffusion in Pd and Ni was calculated by both methods. It was found that the over-barrier diffusion of hydrogen in fcc metals takes place through successive penetration of hydrogen through the octahedral and tetrahedral holes, and that the migration activation energy for transition from the octahedral to the tetrahedral hole is nearly zero. That is why, in the static method, the migration activation energy was calculated as the difference of the energies of the computational cells with the hydrogen atom in the center of the triangle formed by the three neighboring atoms of (111) plane (pass point) and with the hydrogen atom in the octahedral hole. Before the calculations the computational cell was subjected to dynamic relaxation followed by quenching to 0 K.

In the dynamical calculation of the migration activation energy, one hydrogen atom was introduced into the computational cell. The hydrogen diffusion coefficient in metals was estimated for different temperatures. Each computational run was at least 200 ps long with the time step of 1 fs. The diffusion coefficients were calculated from

$$D = \frac{1}{6tN} \sum_{i=1}^N \left((x_{0i} - x_i)^2 + (y_{0i} - y_i)^2 + (z_{0i} - z_i)^2 \right), \quad (6)$$

where x_{0i} , y_{0i} , z_{0i} are the initial coordinates of the hydrogen atom and x_i , y_i , z_i are the coordinates at time t . To exclude the effect of thermal fluctuations, at the end of the computational run the computational cell was quenched to 0 K.

In Fig. 2 the dependencies $\ln D(T^{-1})$ calculated for a single hydrogen atom in the computational cell are given for Pd and Ni.

The concentration of hydrogen atoms in metals can be, of course, different. In order to have the possibility to compare the obtained simulation results with the experimental data, when calculating the the pre-exponent using (5), we took the hydrogen concentration as in the works [3, 17, 26-29], on average, 0.5 % for Pd and Ni.

In Fig. 3 we plot the Pd-H and Ni-H potentials developed in this work. In Table 1 the experimental data used for fitting the potential parameters are presented together with the values found from molecular dynamics simulations based on the offered potentials. The cut-

off radius of the H-H, Pd-H and Ni-H Morse potentials was set to take into account the first five coordination shells (i.e, approximately, $6 \div 6.5 \text{ \AA}$). Table 2 gives the potential parameters.

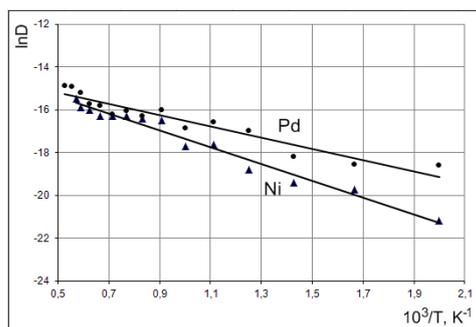


Fig. 2. $\ln D$ as the function of T^{-1} for Pd and Ni for a single hydrogen atom in the computational cell.

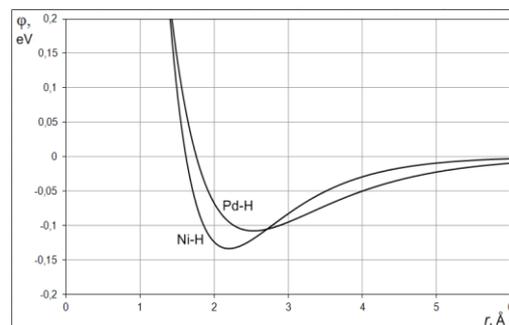


Fig. 3. Pd-H and Ni-H potentials.

Table 1. The hydrogen absorption energy E_{ab} , the vacancy-hydrogen binding energy E_{bv} , the diffusion activation energy E_m and the pre-exponential factor D_0 for Pd-H and Ni-H systems. Experimental data is compared to the molecular-dynamics simulations based on the potentials constructed in this work.

		E_{ab} , eV	E_{bv} , eV	E_m , eV		D_0 , m^2/s
				Static method	Dynamic method	
Pd-H	Experiment	$-0,08 \div -0,12$	$0,25 \div 0,27$ [31-33]	$0,22 \div 0,25$ [3, 17, 26, 27]		$2 \cdot 10^{-7} \div 8 \cdot 10^{-7}$ [3, 17, 26, 27]
	Simulations	-0,100	0,262	0,235	0,23	$9,2 \cdot 10^{-7}$
Ni-H	Experiment	$0,15 \div 0,17$ [3, 7, 8]	$0,32 \div 0,54$ [7, 34]	$0,33 \div 0,42$ [27-29]		$5 \cdot 10^{-7} \div 9 \cdot 10^{-7}$ [27-29]
	Simulations	0,160	0,401	0,375	0,34	$15,1 \cdot 10^{-7}$

Table 2. Morse potential parameters for the H-H, Pd-H and Ni-H interactions.

	α , \AA^{-1}	β	D , eV
H-H	1,3	6,5	0,045
Pd-H	0,9	9,76	0,10737
Ni-H	1,2	14	0,1331

4. Conclusion

The potentials developed in the present study to describe the interaction of hydrogen with palladium and with nickel describe well such experimentally measured quantities as the absorption energy, the over-barrier hydrogen diffusion energy in metals (at room and higher temperatures), the vacancy-hydrogen binding energy. The H-H interactions were constructed taking into account the results of first-principle simulations obtained by other authors.

The developed potentials can be used for molecular dynamics and molecular quasi-static simulations of the Pd-H and Ni-H systems that include large number of atoms and various defects of crystal lattice.

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