

THE STUDY OF THE INTERACTION OF HYDROGEN IMPURITY WITH POINT AND LINEAR DEFECTS IN PALLADIUM AND NICKEL

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Abstract. The work is devoted to the study of the interaction of hydrogen with point defects (vacancy, bivacancy, trivacancy, stacking fault tetrahedron, intrinsic interstitial atom) and linear (complete and partial edge dislocations, screw dislocation) defects in Pd and Ni by the method of molecular dynamics. The bond energies of the hydrogen impurity with considered defects were obtained. It is shown that the most effective hydrogen traps in Pd and Ni are vacancies and vacancy clusters. The high sorption capacity of vacancies should contribute to significantly effect of their concentration on the overall sorption capacity of the metal, especially for metals such as Ni, for which the energy of absorption by vacancies and vacancy clusters is negative while the absorption energy by a pure crystal is positive. The presence of dislocations and dislocation complexes in Ni, low-angle grain boundaries, according to the obtained data, weakly affects to the sorption ability of the metal in comparison with vacancies and vacancy clusters.

Keywords: molecular dynamics; metal; hydrogen; point defect; bond energy; absorption energy; dislocation; stacking fault tetrahedron.

1. Introduction

Interaction of hydrogen with metals remains a topic of active studies in the last century. On the one hand, 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 [1].

The traps, which are responsible for capturing hydrogen atoms in technically pure metals, are lattice defects: point defects and their complexes, dislocations, grain boundaries, volume defects. The researchers note that the most effective traps are grain boundaries, dislocations and vacancies [2]. The interaction of hydrogen with these defects is the reason of a number of phenomena associated with changes in the properties of hydrogenated metals, such as embrittlement, change of and mobility of defects caused by this change in the self-diffusion characteristics of the metal. On the other hand, directional introduction of the traps is an effective way of dealing with hydrogen embrittlement [2]. Therefore, the study of processes of hydrogen interaction with the structure imperfections is topical. Nowadays an open question remains on quantifying sorption capacity with respect to hydrogen of different lattice defects.

In addition to the defects mentioned above, there are unique vacancy clusters in fcc crystals are of the interest - stacking fault tetrahedrons (SFT). At present, it is reliably established that small vacancy clusters in fcc metals are mainly stacking fault tetrahedrons

[3, 4]. The faces of the stacking fault tetrahedron (Fig. 1) are oriented along the $\{111\}$ planes and are stacking faults, and the edges are oriented along the $\langle 110 \rangle$ directions and are partial dislocations with the $1/6\langle 110 \rangle$ Burgers vector [3, 5, 6]. SFTs are formed in all fcc metals, but their critical size, at which the vacancy disks become energetically more advantageous, depends to a large extent on the formation energy of the stacking fault in a given metal [6]. In connection with this, the first SFTs were observed in metals with a low energy of stacking fault (Au, Ag, Cu, etc.) [5, 6]. For example, in Au vacancy disks are observed predominantly above a certain size – 230 Å, while the SFT – up to a size of 200 Å [6]. SFTs are formed as a result of radiation damage, rapid cooling from high temperatures, plastic deformation.

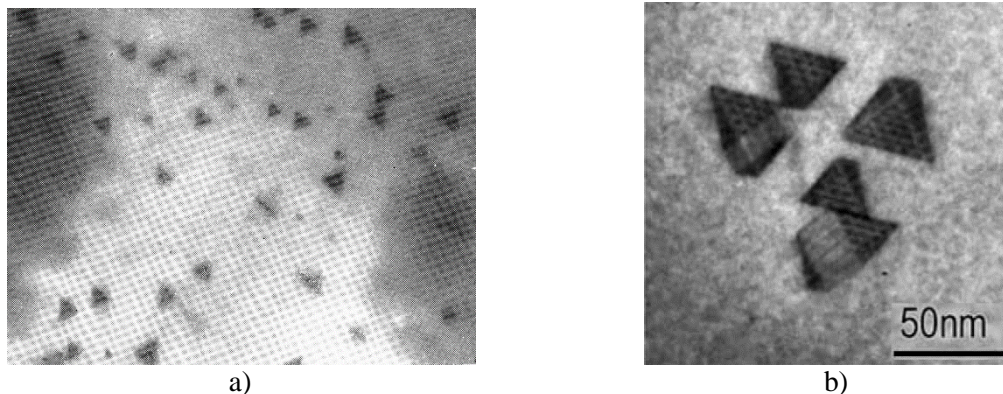


Fig. 1. Stacking fault tetrahedrons in gold observed with the help of an electron microscope: a) the view along the $\langle 111 \rangle$ direction, $\times 10^5$ [5]; b) the group of SFTs [3].

Investigation of the interaction of hydrogen impurities with different structure defects at the atomic level is in its initial stages and is preferably carried out using methods of computer simulation. The present work is devoted to the study of interaction of hydrogen with point defects (vacancy, bivacancy, trivacancy, stacking fault tetrahedron, intrinsic interstitial atom) and linear (complete and partial edge dislocations, screw dislocation) defects in Pd and Ni by the method of molecular dynamics. Selecting of fcc metals Pd and Ni is due to an increased attention to them and a relatively large amount of the available experimental data for these metals. Palladium has an extremely high sorption capacity relative to hydrogen, the absorption energy (the work that must be expended to put one hydrogen atom in the metal taking into account work H-H bond breaking in a diatomic molecule of hydrogen H_2) is negative and amounts to -0.1 eV [7, 8]. Nickel belongs to metals with an average adsorption capacity. The absorption energy is positive for this metal, but a small and amounts to 0.16 eV [2, 9]. Earlier, we conducted studies of the interaction of hydrogen impurity with vacancies and interstitial atoms [10], edge dislocations [11] and low-angle twist boundaries [12]. In the present work these results are combined and supplemented by studies of the interaction of hydrogen with bivacancies, trivacancies, stacking fault tetrahedrons and partial dislocations.

2. Description of the model

The calculation blocks in the computer model included 8400 atoms. The boundary conditions were used periodically. The vacancy was introduced by removing the atom from the calculation block. Bivacancy (two combined vacancies) was created by removing two neighboring atoms located along the close-packed direction and subsequent relaxation. Trivacancy (three combined vacancies) and SFTs were created by introducing "triangular vacancy disks." Additional thermal activation was not required to form a SFT from vacancy disks of triangular shape. The mechanism of the "triangular vacancy disks" rearranging in the $\{111\}$ plane to the SFT consisted of successively displacing (settling) of groups of atoms in the form of an equilateral triangle from the planes parallel to the vacancy disk plane toward it (Fig. 2). Because

of the peculiarities of the fcc lattice, the sizes of the shifting groups of atoms of a triangular shape were successively decreased, as a result of which the free volume of the initial vacancy disk propagated into the tetrahedral region of the crystal and almost uniformly distributed inside the SFT with an insignificant increase in its concentration in the defect boundary region.

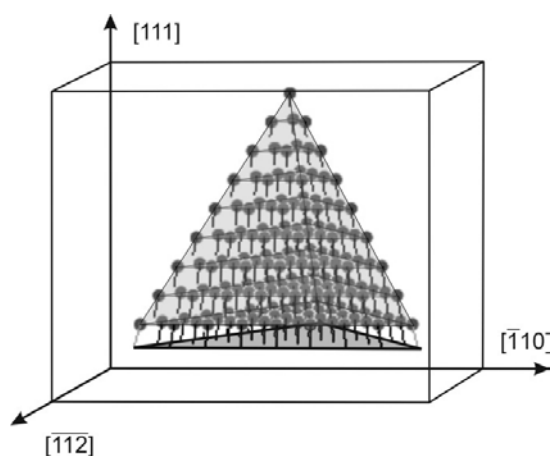


Fig. 2. Formation of the SFT from the "triangular vacancy disk": displacements (shown by segments) of groups of triangular atoms from neighboring planes towards the vacancy disk.

The hydrogen atom was introduced into the computational block at various positions relative to the considered defect. In each case structural relaxation was carried out, at the end of which the calculation block was cooled to 0 K in order to exclude the effect of thermal displacements of atoms in calculating of the energy characteristics of the hydrogen impurity. Structural relaxation was carried out by the method of molecular dynamics. The time step in molecular dynamics experiments was 1 fs. The interactions of metal atoms with each other were described by the many-particle Clery-Rosato potential [13]. The experience of applying of this potential shows that with its help it is possible to describe the various properties of metals [12-17]. The H-H, Pd-H and Ni-H interactions were described using the Morse potentials found in [17] by the absorption energy, the activation energy of hydrogen diffusion (at normal and high temperatures) and the binding energy with the vacancy.

3. Results and discussion

The main energy characteristics describing the interaction of hydrogen with point defects are the binding energy of hydrogen with a defect and the energy of hydrogen absorption by a defect. The binding energy of hydrogen with a point defect E_b was calculated in the present work as the difference in the potential energy of the calculation block containing the considered defect and the hydrogen atom in the octahedral pore (in the fcc lattice, as is known, hydrogen is predominantly located in the octahedral pores [1, 2, 7]) on such a distance from each other which eliminates the interaction of the point defect and the hydrogen atom, and the potential energy of the calculation block containing the hydrogen atom in the defect. Different positions of hydrogen atom in a defect were considered. Wherein the maximal value of all binding energies was chosen, indicating about the most energetically favorable position of hydrogen in the defect.

The energy of hydrogen absorption by a defect is the work that must be spent to put one hydrogen atom from infinity into the defect region taking into account the work of breaking the H-H bond in the diatomic hydrogen molecule H_2 (it is known that hydrogen molecules H_2 in the metal volume dissociate into individual atoms due to significant attenuation covalent bond – in metals, in the crystal lattice and in the region of defects hydrogen is in the atomic state [2]). The energy of hydrogen absorption by a point defect was calculated by formula:

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

where U_0 – potential energy of metal crystal containing considered defect taking into account the relaxation of the atomic structure; U_H – potential energy of the crystal containing a hydrogen atom in the defect region; E_{dis} – dissociation energy of hydrogen molecule H_2 ($E_{dis} = 4.485$ eV [2]).

Fig. 3 shows the positions of the hydrogen atom in the trivacancy and the SFT for which the binding and absorption energies were calculated. All obtained values of E_b and E_{ab} for point and linear defects in Pd and Ni are given in Table 1. The data from other works are indicated in parentheses in the table.

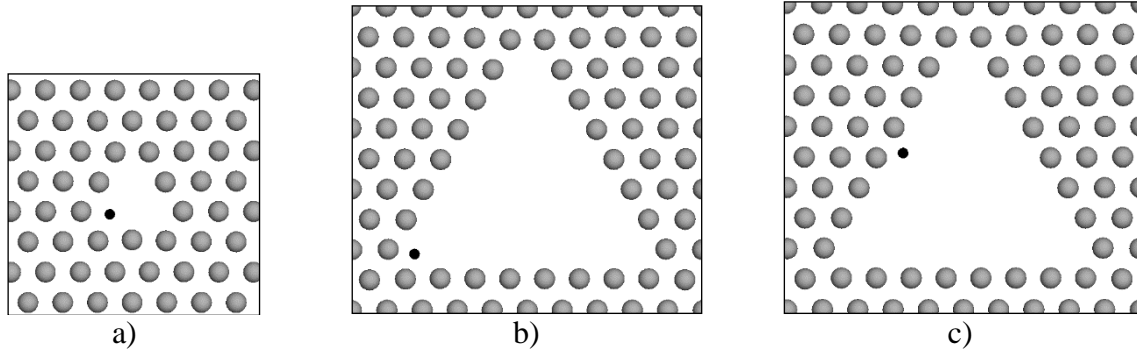


Fig. 3. The positions of the hydrogen atom shown in the section in which the SFT or the trivacancy face lies: a) in the trivacancy; b) at the top of the SFT; c) on the edge of the SFT.

Table 1. The binding energy of hydrogen with a defect E_b and the energy of hydrogen absorption by a defect E_{ab} in Pd and Ni.

	Pd		Ni	
	E_b , eV	E_{ab} , eV	E_b , eV	E_{ab} , eV
vacancy [10]	0.262 (0.25-0.27 [18, 19])	-0.362	0.401 (0.32-0.54 [9,20])	-0.241
bivacancy	0.172	-0.272	0.310	-0.150
trivacancy	0.105	-0.205	0.229	-0.069
SFT top	0.106	-0.206	0.197	-0.037
SFT edge ($1/6\langle 110 \rangle$ partial dislocation)	0.003	-0.103	0.105	0.055
interstitial atom [10]	0.041	-0.141	0.095	0.065
$1/2\langle 110 \rangle$ edge dislocation [11]	0.21 (0.19 – 0.22 [21])	-0.31	0.16 (0.09 – 0.15 [22])	0
kink on $1/2\langle 110 \rangle$ edge dislocation [11]	0.23	-0.33	0.23	-0.07
$1/2\langle 110 \rangle$ screw dislocation [12]	0.01	-0.11	0.01	0.15

When one hydrogen atom was introduced into vacancy there were obtained the binding energies E_b : 0.262 eV for Pd and 0.401 eV for Ni. Since this quantity was one of the parameters by which the potentials of the interaction of metal atoms with a hydrogen atom were selected in [17], the obtained values are in complete agreement with the known experimental data: 0.25-0.27 eV for Pd [18, 19] and 0.32-0.54 eV for Ni [9, 20].

Good agreement with the data of other authors is also observed for the binding energy of hydrogen with edge dislocation. We obtained the following values: 0.21 eV for Pd and 0.16 eV

for Ni. Very close values are given in [21, 22]: 0.19-0.22 eV [21] for Pd and 0.09-0.15 eV [22] for Ni. The binding energy of the hydrogen atom with the kink (step or threshold) on the edge dislocation is higher than with an uncorrelated dislocation core: 0.23 eV for Pd and Ni.

With $1/6\langle 110 \rangle$ partial dislocation, which is also an edge of the SFT, the binding energy is lower than with the nucleus of a complete dislocation. It is energetically more advantageous for the hydrogen atom to be located in the top of the SFT than in any other place in the SFT. At the same time, as can be seen from the table, the binding energy with the SFT top is almost the same as with the trivacancy, which indicates about a similar arrangement of atoms near the top of the SFT and the complex of three vacancies.

The sorption capacity of bivalencies relative to hydrogen, according to the obtained data, is between the sorption capacity of vacancies and trivacancies. In general, the most effective trap for hydrogen among the considered defects is a vacancy. The binding energy of hydrogen with dislocations turned out to be lower than for vacancies, especially for Ni. The high sorption capacity of vacancies should contribute significantly to the effect of their concentration on the overall sorption ability of the metal. For example, for a pure Ni crystal, the absorption energy is positive (0.16 eV [2, 9]), i.e. placing hydrogen in a Ni crystal is energetically disadvantageous and in a state of thermodynamic equilibrium the hydrogen concentration in Ni is low, usually a tenth of a percent [2]. However, the energy of absorption by vacancies and vacancy clusters, according to the obtained data, is negative. This means that the sorption capacity of such metals as Ni should strongly depend on the concentration of vacancies. For Pd, for which the absorption energy by a pure crystal is negative enough (-0.1 eV [7, 8]), the effect of vacancies should apparently be less significant.

4. Conclusion

With the help of the molecular dynamics method, there were obtained the binding and absorption energies of hydrogen by point (vacancy, bivacancy, trivacancy, stacking fault tetrahedron, intrinsic interstitial atom) and linear (complete and partial edge dislocations, screw dislocation) defects in Pd and Ni. It is shown that the most effective hydrogen traps in Pd and Ni are vacancies and vacancy clusters. The high sorption capacity of vacancies should contribute to significantly effect of their concentration on the overall sorption capacity of the metal, especially for metals such as Ni, for which the energy of absorption by vacancies and vacancy clusters is negative while the absorption energy by a pure crystal is positive. The presence of dislocations and dislocation complexes in Ni, low-angle grain boundaries, according to the obtained data, weakly affects to the sorption ability of the metal in comparison with vacancies and vacancy clusters.

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