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MOLECULAR DYNAMICS SIMULATION OF INTERACTION OF HYDROGEN IMPURITY WITH TWIST BOUNDARIES IN Pd AND Ni

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Abstract. The study of the interaction of hydrogen impurity with (100) and (111) twist boundaries in Ni and Pd was held by the method of molecular dynamics. It is shown that twist boundaries may act as hydrogen traps, but less effective in comparison with vacancies and edge dislocations. The energy of the hydrogen connection with the twist boundary, according to the obtained data, does not exceed 0.1 eV for both metals.

1. Introduction

Interaction of hydrogen with metals remains a topic of active studies in the last century. 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.

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 twist grain boundaries 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 [3, 4]. 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, 5]. In [6, 7] we have shown that in the case of hydrogen sorption by a vacancy and an edge dislocation the absorption energy for nickel becomes negative (-0.1 to -0.17 eV respectively), which indicates the possibility of a significant increase in the sorption capacity of nickel when introduced a high concentration of the defects.

2. Description of the model

The simulation was held using the method of molecular dynamics. A twist boundary was created in the middle of the calculation block by rotating of the two fcc crystals (two block halves) on misorientation angle θ around an axis perpendicular to the boundary (Fig. 1). Two variants of boundary plane were considered (in Fig. 1 boundary plane allocated in gray): (100) and (111). The resulting calculation block truncated so that it has acquired a parallelepiped shape and did not contain voids at the edges (in the figure the final calculation block marked by a dotted contour). Then dynamic relaxation of the structure was carried out, during which bicrystal passed to an equilibrium state, and temperature of the calculation block increased. At the end of the relaxation procedure was carried out cooling to 0 K.

Boundary conditions were rigid on all axes, ie extreme atoms of the calculation block remained motionless during the process of computer experiment. This type of conditions allows to keep the position of grain boundary with given initial geometrical parameters. The number of atoms in the calculation block was about 30,000.

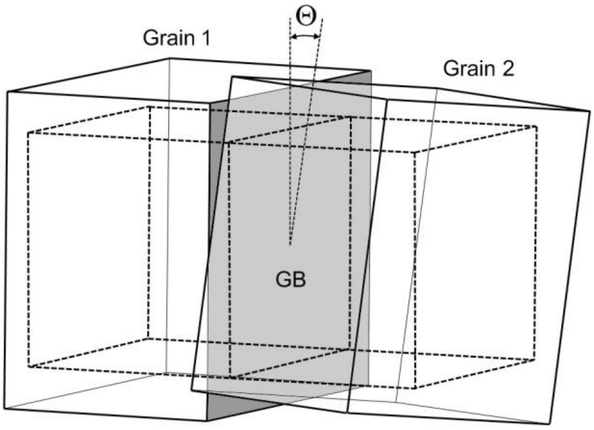


Fig. 1. The scheme of creation of the calculation block with twist grain boundary. θ - the misorientation angle; GB - grain boundary (the boundary plane allocated in gray).

In [8] it is shown that the low-angle twist boundaries have an ordered structure, which represents a network of screw dislocations. In [8], we carried out the identification of screw dislocations in (100), (110), (111) twist boundaries in fcc metals on example Ni, Cu, Al. It is shown that (100) boundaries contain square network of 1/2<110> screw dislocations, (111) boundaries – triangular network of 1/4<112> screw dislocations. With increase in the misorientation angle the cell sizes of dislocation network decreased. Atomic structure in the center of the network cells corresponds to ideal crystal.

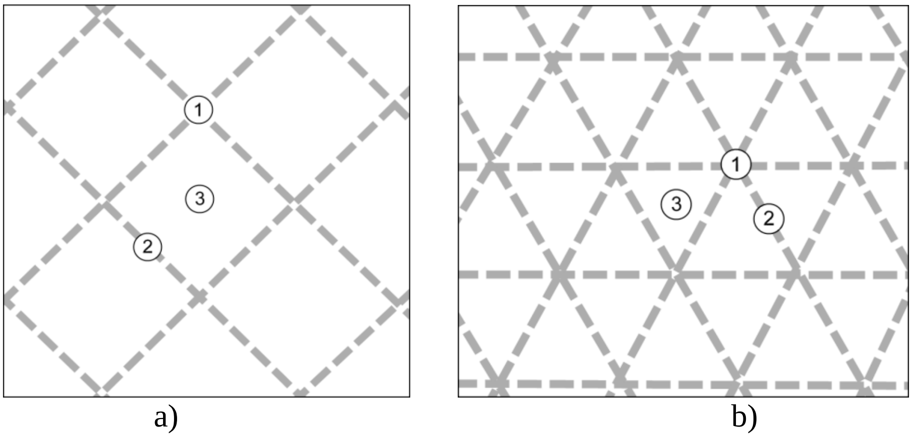
After creating the calculation block containing a twist boundary, subsequent relaxation of the structure and cooling, hydrogen atoms were introduced. When studying the hydrogen bond energy with grain boundary one hydrogen atom was introduced in different positions on the boundary. To study the distribution of hydrogen impurities due to diffusion a certain concentration of randomly distributed in the calculated block hydrogen atoms was introduced; the value of the hydrogen concentration could be varied.

Time integration step of movement of metal atoms in the molecular dynamics method was equal to 5 fs, of hydrogen atoms − 0.5 fs. The interactions of metal atoms with each other (Pd-Pd and Ni-Ni) were described by Clery-Rosato many-particle potentials which were built in [9] within the tight-binding model. This potential has well recommended itself in a number of calculations of structural and energy characteristics of metals, made by the method of molecular dynamics [9-12]. To describe the H-H, Pd-H, Ni-H interactions pair Morse potentials were used, the parameters of which were taken from [10], where they were calculated using experimental data on the absorption energy, the activation energy of over-barrier diffusion of H in metals (at normal and high temperatures), the H-vacancy binding energy.

3. Results and discussion

In the process of structural relaxation, during which conjugation of crystal grains occurred, the networks of screw grain boundary dislocations formed on low-angle boundaries: square network of 1/2<110> screw dislocations on (100) boundaries (Fig. 2a) and triangular network of 1/4<112> screw dislocations on (111) boundaries (Fig. 2b).

The main energetical characteristics describing the interaction of hydrogen with the considered defect are the binding energy of hydrogen with the defect and the absorption energy. The binding energy of hydrogen with a twist boundary calculated as the difference in the potential energy of calculation block containing the boundary and a hydrogen atom in the octahedral pore at a distance from each other, which eliminates the interaction of boundary and hydrogen, and the potential energy of calculation block containing of hydrogen atom in a given position in the considered boundary. In both cases, the dynamic relaxation was carried out before the calculation of energy of the simulation block, after which the simulation block was cooled to 0 K. In other words, the binding energy of hydrogen with a defect is work that must be expended to remove a hydrogen atom from a defect to an octahedral pore of pure fcc crystal (in an octahedral pore hydrogen atom has minimal energy compared to other positions in fcc crystal) [10].



a) b)

Fig. 2. The networks of grain boundary screw dislocations on low-angle twist (100) (a) и (111) (b) boundaries. Gray bold dotted lines show the positions of screw dislocations. The numbers marked the different positions in which hydrogen was introduced: 1 – node of dislocation network, 2 - core of screw dislocation, 3 - the center of dislocation network cell.

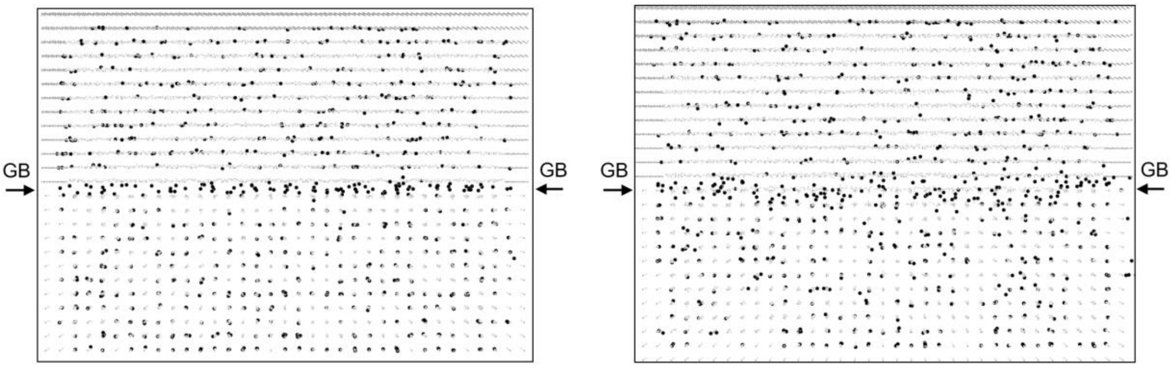
To analyze the sorption capacity of low-angle boundaries the binding energy was calculated at the introduction of hydrogen in various positions in the boundary: in a node of the dislocation network, in a core of a screw dislocation, in the center of a cell of the dislocation network (Fig. 2). In the case of high-angle boundaries hydrogen was introduced in different random places. Table 1 shows the results of highest values of the binding energy with 7° and 30° twist boundaries in Ni and Pd. In the center of cells of the grain boundary dislocations network the structure represents an ideal crystal and energy of hydrogen in this position (position 3 in Fig. 2) does not differ from the energy in the pure crystal.

Table 1. Highest values of the binding energy of hydrogen with twist boundaries in Ni and Pd, eV.

Metal	Boundary	Low-angle boundary (7°)		High-angle boundary (30°),
		Node of dislocation network	Core of screw dislocation	
Ni	(100)	0.07	-0.01	0.09
	(111)	0.02	0.02	0.05
Pd	(100)	0.09	-0.01	0.10
	(111)	0.02	0.02	0.04

As seen from the table, the twist boundaries have a relatively low sorption capacity with respect to hydrogen. The highest values of the binding energy of hydrogen with the considered boundaries are several times less binding energy with the vacancy (0.40 eV in Ni and 0.26 eV in Pd [6]) and edge dislocation (0.16 eV in Ni and 0.21 eV in Pd [7]). In the case of the low-angle boundaries the highest energy was observed at introduction of hydrogen in the nodes of the dislocation network.

To study the interaction of freely diffusible hydrogen in a metal with the considered boundaries a high concentration of hydrogen of 5 % was introduced to the calculation blocks. This concentration exceeds in dozens times the concentration that typically is observed in real experiments [13]. This was done to facilitate the analysis of distribution of hydrogen impurities in the area of grain boundary. After the introduction of hydrogen atoms the molecular dynamics experiment was carried out for 300 ps at step temperature decreases from 700 K to 200 K (for the analysis of the effect of temperature on distribution of hydrogen). In the process of the computer experiment hydrogen atoms diffused freely in the calculation block. Figure 3 shows the final result in the case of high-angle (100) boundaries in Ni and Pd: black dots indicate hydrogen atoms, gray - metal atoms.



a) b)

Fig. 3. The distribution of hydrogen in area of (100) 30° in Ni (a) and Pd (b) twist boundaries after the computer experiment during 300 ps at step temperature decreases from 700 K to 200 K. Black dots indicate hydrogen atoms, gray - metal atoms. GB – grain boundary.

As seen in Fig. 3, despite the relatively low binding energy, hydrogen still lingers and accumulates on the boundary during migration, indicating that the twist boundaries can act as hydrogen traps. Behavior of hydrogen near the boundaries in Ni and Pd has a difference. In boundaries in Pd hydrogen more "blurred", is not concentrated as in Ni. Apparently, this is due to the lower value of absorption energy of hydrogen in pure Pd crystal compared with Ni.

4. Conclusion

In the present work, the study of the interaction of hydrogen impurity with (100) and (111) twist boundaries in Ni and Pd was held by the method of molecular dynamics. It is shown that binding energy of hydrogen with the considered boundaries is low and does not exceed 0.1 eV (in case of absence excess defects on the boundary) for both metals, which is considerably lower than binding energy of hydrogen with the vacancies and edge dislocations. In the case of low-angle boundaries, highest binding energy corresponds to the position of hydrogen in the nodes of the grain boundary dislocations network.

Using molecular dynamic experiment it is shown that the hydrogen in the diffusion process delays and accumulates in the twist grain boundaries, which suggests about the ability to twist boundaries act as hydrogen traps, but, apparently, due to the relatively low binding energy of hydrogen with them, less effective than tilt boundaries.

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