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INTERACTION OF IMPURITY ATOMS OF LIGHT ELEMENTS WITH VACANCIES AND VACANCY CLUSTERS IN FCC METALS

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Abstract. The interaction of impurity atoms of light elements C, N, O with vacancies and vacancy clusters in fcc metals Ni, Ag and Al was studied by the molecular dynamics method. The binding energies of impurity atoms with vacancies, divacancies and stacking fault tetrahedron (SFT) are calculated. It is shown that the impurity atom in a vacancy is not located at its center, but is displaced relative to it in the direction of the <100> type. The changes in the activation energy of vacancy migration upon interaction with an impurity atom are calculated. When studying the interaction of impurity atoms with a SFT, it was found that the binding energy of C, N and O atoms for all the considered metals is higher with the SFT edge (i.e. with partial dislocation) than with the top of the SFT.

Keywords: molecular dynamics, metal, vacancy, impurity, binding energy, divacancy, vacancy cluster, stacking fault tetrahedron

1. Introduction

Impurity atoms of light elements (primarily the most common ones: hydrogen, oxygen, nitrogen, carbon) have high chemical activity and already at low concentrations strongly influence on the properties of metals. Being effective stoppers of dislocations and grain boundaries, the impurities of light elements significantly increase the strength, hardness, frictional properties simultaneously, as a rule, with brittleness [1-3]. A high melting temperature and chemical resistance are typical for many interstitial alloys. Despite the importance of understanding the mechanisms and processes underlying the effect of doping light elements on the properties of metals, now there are many questions regarding the behavior of impurities at the atomic level in the metallic matrix. In particular, the questions of interaction at the atomic level of various interstitial impurities with defects in the crystal lattice, especially dislocations and grain boundaries, remain insufficiently studied. In this case, computer simulation is an effective research tool.

This work is devoted to the study using molecular-dynamic modeling of the interaction of impurity atoms of light elements C, N and O with vacancies and vacancy clusters in metals with fcc lattice. As metals, Ni, Ag and Al were chosen. This set of three metals is unique in that two of them have almost the same radii of atoms, while the other two have almost identical electronegativities. The radii of atoms: Al − 1.43 Å, Ag − 1.44 Å, Ni − 1.24 Å [1]. Electronegativity (Pauling scale): Al − 1.61, Ag − 1.93, Ni − 1.91 Å [3]. Thus, when obtaining different dependencies for these three metals, the relationship either with the size of atoms or with electronegativity will be seen.

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2. Description of the model

The simulation was performed using the molecular dynamics method. The calculation block of the crystal had the shape of a parallelepiped and contained 8400 atoms. Periodic boundary conditions were used. Interactions of metal atoms with each other were described by the EAM tight-binding Cleri-Rosato potentials [4]. In this case, the energy of the *i*-th atom is found using expression:

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

Here A, p, q, ξ, r_0 are the potential parameters; r_{ij} is the distance between the *i*-th and *j*-th atoms. The parameters of the Cleri-Rosato potentials were taken from [4].

To describe the interactions of impurity atoms of light elements with metal atoms and impurity atoms with each other the Morse potential was chosen:

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

where α, β, D are the parameters of the potential. Cleri-Rosato and Morse potentials have proved themselves in numerous calculations performed by the molecular dynamics method [5-8]. Pair potentials are relatively often used by various researchers to describe interatomic interactions in metal-impurity systems. Multi-particle potentials are physically more reasonable, but taking into account the high error of the experimental data on which the potential parameters are selected, as well as the error of the search methods of the parameters themselves, the choice of pair potentials is justified.

The parameters of the potentials for describing the interactions of impurity atoms C, N and O with the metal atoms under consideration were taken from [9], where they were found taking into account empirical dependencies and known characteristics, such as the melting or decomposition temperature of the corresponding chemical compound of a metal with a light element, activation energy of the diffusion of an impurity atom in the crystal lattice of the metal. In [9], to describe the interactions of impurity atoms with each other in metals, the potentials proposed by other authors have been taken as a basis. For the C-C bond, the pair potential from [10] was transformed into Morse potentials. For N-N and O-O bonds, potentials were taken from [11,12].

3. Interaction of impurity atoms with vacancies

The binding energy of an impurity atom with a vacancy E_{bv} was calculated as the difference between the potential energy of a calculation block containing a vacancy and an impurity atom at such a distance from each other, which eliminates their interaction, and the potential energy of a calculation block containing an impurity atom inside a vacancy. In both cases, before the calculation of the energy of the computational block, the structure was relaxed, after which the calculation block was cooled to 0 K.

When conducting structural relaxation of the calculation block containing an impurity atom inside a vacancy, it was observed that the impurity atom in the vacancy is not located at its center, but is displaced relative to it in the direction of the <100> type. In Table 1, in addition to the binding energy of an impurity with a vacancy, the values of the displacement of the impurity atom δ from the center of the vacancy are shown (Fig. 1).

In the literature there is very little information on the binding energy of light-element atoms with defects of the crystal lattice of metals. For fcc metals, we found only the binding energy of a carbon atom with a vacancy in γ-Fe: 0.67 eV [13] and 0.37–0.41 eV [14]. In [14], this quantity was found experimentally and with the help of ab-initio calculations; in [13] – only by the calculations. Of the metals under consideration, the characteristics of γ-Fe are closest to Ni (atomic radii: 1.29 Å (γ-Fe) and 1.24 Å (Ni); differences of electronegativities

with carbon: 0.72 (Fe) and 0.64 (Ni)). The binding energy of a carbon atom with a vacancy in nickel, found in our model, turned out to be 0.70 eV, which is close to the values in [13].

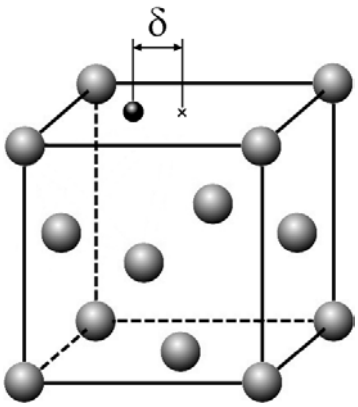


Fig. 1. The displacement of the impurity atom δ from the vacancy center (the vacancy center is marked with a cross)

Table 1. The binding energy of an impurity atom with a vacancy (eV)

	C		N		O	
	E_{bv}	δ (Å)	E_{bv}	δ (Å)	E_{bv}	δ (Å)
Ni	0.70	0.44	0.39	0.68	-0.05	0.80
Ag	0.05	1.03	-0.25	1.24	-0.59	1.97
Al	0.86	0.95	0.14	1.00	-0.58	1.05

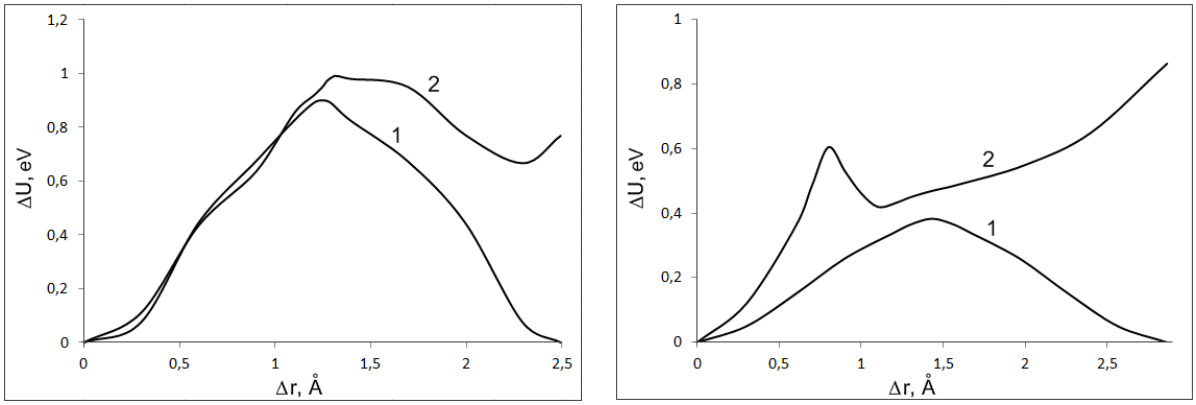
According to the data obtained in the work, the binding energy of impurity atoms with a vacancy is not always positive. For example, negative values were obtained for the oxygen atom for all three considered metals. This means that between a vacancy and an impurity oxygen atom there must be a kind of repulsion, their combination is energetically unfavorable. The largest values of the binding energy with a vacancy are obtained for a carbon atom in Ni and Al, which is apparently related to the largest size of carbon atoms among considered impurities. The smallest values of the binding energy and at the same time the largest displacements of impurity atoms from the center of the vacancy δ were obtained for Ag. In this case, impurity atoms are shifted almost to the position of the neighboring octahedral pore.

Thus, vacancies are a "trap" mainly for relatively large impurity atoms, for example, carbon. For atoms of small size, such as, for example, oxygen, combining with vacancies is energetically not beneficial.

In this work, we also investigated the effect of impurity atoms on the diffusion of vacancies in the metals under consideration. The migration energy of a vacancy was determined by the magnitude of the energy barrier in the migration path of the defect. In addition to the migration of a "pure" vacancy, the migration energies of a vacancy in the presence of an impurity atom in it were calculated. To obtain each point on the graph of the change in the energy of the calculation block, the structure was relaxed, during which the displaced atom, adjacent to the vacancy, remained stationary. Figure 2 shows the dependences of the change in the energy of the calculation block ΔU on the displacement Δr of an atom adjacent to a vacancy in the case of the vacancy without impurity (graph 1) and with an impurity carbon atom (graph 2).

The graphs obtained for a vacancy with an impurity carbon atom, as can be seen from Fig. 2, asymmetric, in contrast to the graphs for vacancies without impurities. Nevertheless, the extremum is distinct and it is possible to estimate the activation energy of vacancy

migration with its separation from the impurity atom. It should be noted that the peak at the 2nd dependence in Fig. 2 is located to the right of the peak for the "pure" vacancy in the case of Ni and to the left in the case of Al.



a) b)

Fig. 2. The change in the energy of the calculation block when an atom adjacent to a vacancy moves to its place: a) in Ni, b) in Al. 1 – in pure metal. 2 – in the case of the presence of an impurity carbon atom in the vacancy

Table 2 shows the values obtained in the present work for the migration energy of a vacancy with and without impurities. These values are obtained for the "separation" of vacancies from impurities, not for the case of joint movement of vacancies and impurities. For joint migration of vacancy and impurity, it is necessary to implement an additional mechanism consisting in the exchange of places of the metal atom and impurity atom adjacent to the vacancy.

Table 2. The migration energy of a vacancy with and without an impurity atom (eV)

	without impurity	C	N	O
Ni	0.90	0.99	0.78	0.52
Ag	0.91	0.81	0.74	0.87
Al	0.38	0.60	0.61	0.26

The obtained values of the migration energy of a vacancy in a pure metal are in satisfactory agreement with the data of other authors. For example, for Ni, values in the range of 0.9–1.1 eV are given in [15,16] and 0.4–0.6 eV for Al.

The effect of impurities on the diffusion mobility of a vacancy is consistent with the previously mentioned binding energies of impurity atoms with a vacancy (Table 1). As can be seen from the Table 2, carbon atoms, having a positive binding energy, inhibit the diffusion of vacancies in Ni and especially in Al. In this case, due to the much higher mobility of vacancies compared to the mobility of impurity atoms [1,9], it seems more correct to say that impurity atoms are a "trap" for vacancies, and not vice versa. Oxygen atoms, on the contrary, "accelerate" the migration of vacancies, reducing their activation energy due to the negative binding energy of oxygen atoms with a vacancy. Nitrogen for different metals has a different effect on the migration of vacancies: it reduces the energy of migration in the case of Ni and Ag and increases it in the case of Al.

4. Interaction of impurity atoms with divacancies and stacking fault tetrahedron

Along with the vacancy mechanism, the contribution to diffusion in crystals is made by the migration of divacancies (bivacancies) – doubled vacancies [15,17]. Even in equilibrium

conditions in crystals there is a small concentration of them (as a rule, approximately two orders of magnitude lower than the concentration of monovacancies). Divacancies are unique in that they are the most mobile among vacancy clusters. In [17], using the molecular dynamics method, the activation energies of divacancy migration were found: 0.23 eV in Ni, 0.18 eV in Ag, and 0.09 eV in Al. As can be seen, these values are several times lower than the energies of monovacancy migration (Table 2). With an increase in the number of vacancies in a cluster, its mobility sharply reduced. The next cluster, trivacancy, has a much lower mobility than mono- and, especially, divacancy [15].

Table 3 shows the binding energy of impurity atoms with divacancies in the metals under consideration. It should be noted that they are close to the values for monovacancies, differing, as a rule, only by the second decimal place. In accordance with these values, as for monovacancies, the influence of impurity atoms on the diffusion mobility of divacancies should be expected.

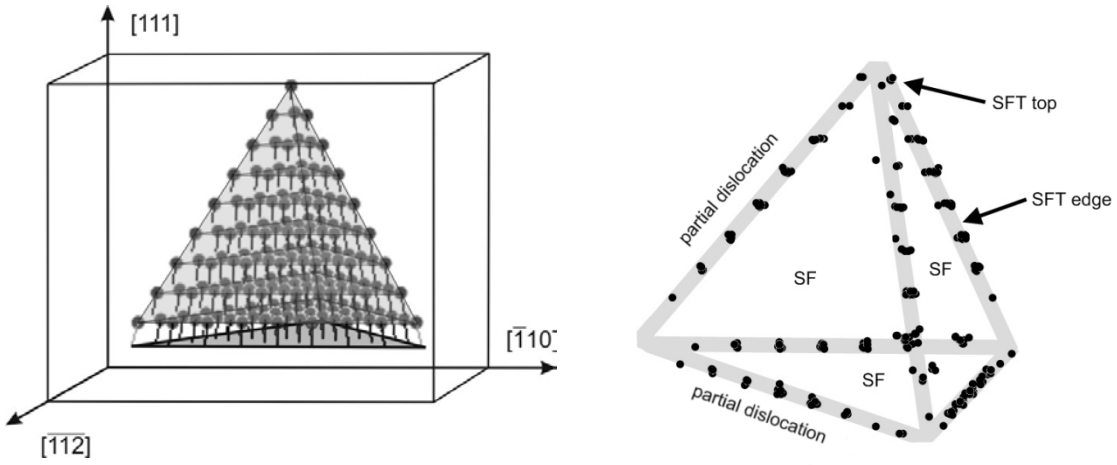
Table 3. The binding energy of an impurity atom with a divacancy (eV)

	C	N	O
Ni	0.76	0.50	0.02
Ag	0.06	-0.23	-0.57
Al	0.89	0.22	-0.28

The role of point defects is not limited to diffusion. With their high concentration in materials, they have a significant impact on the strength properties. Nonequilibrium high concentrations of point defects are formed as a result of rapid cooling from high temperatures, plastic deformation and radiation damage [15,18].

In addition to the defects mentioned above, of interest are unique vacancy clusters in fcc crystals – stacking fault tetrahedrons (SFT). At present, it is reliably established that small vacancy clusters in fcc metals are mainly stacking fault tetrahedrons [19,20]. The faces of the stacking fault tetrahedron (Fig. 3) are oriented along the (111) planes and are stacking faults, and the edges are oriented along the <110> directions and are partial dislocations with the 1/6<110> Burgers vector [19]. 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 [21]. SFTs are formed as a result of radiation damage, rapid cooling from high temperatures, plastic deformation.

In the molecular dynamics model, SFTs were created by introducing "triangular vacancy disks" (Fig. 3a). To do this, atoms were removed from the region having the shape of an equilateral triangle in the close-packed atomic (111) plane. For the formation of a SFT from such a "vacancy disk", additional thermal activation was not required. The mechanism of the "triangular vacancy disks" in the (111) plane to the SFT consisted in successively displacing (settling) of groups of atoms in the form of equilateral triangles from the planes parallel to the "vacancy disk" plane toward it (Fig. 3a). 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 evenly distributed over the edges of the SFT (Fig. 3b). In Figure 3b it was used the visualizator of excess free volume, i.e. free volume over that which is characteristic of a pure crystal. It can be seen, for example, that inside the SFT itself, the structure corresponds to the structure of an ideal crystal, and all the excess free volume is concentrated on the edges of the SFT, which, as already mentioned, are partial dislocations. The faces of a SFT are stacking faults and contain almost as much free volume as an ideal crystal.



a) b)

Fig. 3. Stacking fault tetrahedron in the molecular dynamic model: a) creation of a SFT from a "triangular vacancy disk" (displacements of atoms in the process of structural relaxation are shown by segments); b) the distribution of excess free volume in the SFT

Impurity atoms were introduced in two positions: at the top and edge of the SFT. The values obtained are shown in Table 4. As can be seen from the table, the binding energy of C, N and O atoms for all metals turned out to be higher with the edge of the SFT (i.e. with 1/6<110> partial dislocation) than with the top. In addition, in all cases the binding energies are positive, which indicates the attraction of impurities by such dislocations. The highest binding energy is obtained for a carbon atom with a SFT edge in Al – 1.40 eV. Such a high value of the binding energy speaks in favor of a relatively strong bond of carbon atoms with dislocations of this type. The lowest binding energies are obtained for Ag, which is apparently due to two factors simultaneously: a relatively large lattice parameter and not deep interaction potentials of impurity atoms with metal atoms. As in the cases of vacancies and divacancies, the lowest values of the binding energy are obtained for oxygen.

Table 4. The binding energy of an impurity atom with a top and edge of SFT (eV)

	C		N		O	
	top	edge	top	edge	top	edge
Ni	0.64	0.77	0.49	0.72	0.27	0.62
Ag	0.10	0.30	-0.03	0.15	-0.34	0.01
Al	0.80	1.40	0.24	0.88	-0.11	0.44

5. Conclusion

The interaction of impurity atoms of light elements C, N, O with vacancies and vacancy clusters in fcc metals Ni, Ag and Al was studied by the molecular dynamics method. The binding energies of impurity atoms with vacancies, divacancies and stacking fault tetrahedron (SFT) are calculated. It is shown that the impurity atom in a vacancy is not located at its center, but is displaced relative to it in the direction of the <100> type. According to data obtained, vacancies are a "trap" mainly for relatively large impurity atoms, for example, carbon. For atoms of small size, such as, for example, oxygen, combining with vacancies is energetically not beneficial. The changes in the activation energy of vacancy migration upon interaction with an impurity atom are calculated. It is shown that at the positive binding energy of an impurity atom and a vacancy, they inhibit the migration of each other during the interaction. When studying the interaction of impurity atoms with a SFT, it was found that the binding energy of C, N and O atoms for all the considered metals is higher with the SFT edge (i.e. with partial dislocation) than with the top of the SFT.

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