

THE BINDING ENERGY OF IMPURITY ATOMS C, N, O WITH EDGE DISLOCATIONS AND THE ENERGY OF THEIR MIGRATION ALONG DISLOCATION CORE IN Ni, Ag, Al

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Abstract. Using the molecular dynamics method, the binding energies of impurity atoms of light elements C, N, O with edge dislocations, and the energy of their migration along with dislocation core in metals with fcc lattice Ni, Ag, and Al were calculated. The binding energies of impurity atoms with partial and stair-rod dislocations, as well as with jogs on them, were calculated. It is shown that the binding energy with partial dislocations is significantly lower than with stair-rod ones. The binding energy of an impurity atom with a dislocation is determined mainly by two factors: the depth of the interaction potential of the impurity atom with metal atoms and the ratio of their sizes. For this reason, in most cases, the binding energy for carbon with dislocations was greater than for oxygen atoms. The values of the activation energy of the impurity atoms diffusion along a dislocation core were found. The obtained values are several times lower than the activation energy of impurity diffusion in a pure crystal.

Keywords: molecular dynamics, metal, impurity, dislocation, binding energy, activation energy

1. Introduction

Impurities of light elements, such as carbon, nitrogen, oxygen, even at low concentrations strongly affect the mechanical properties of metallic materials. The positive binding energy of impurity atoms with dislocations is the reason for their accumulation at dislocation core and the formation of the so-called Cottrell atmospheres [1-4]. As a result of the diffusion of impurity atoms to the dislocation core, relatively many of them can accumulate near the core, which significantly reduces the mobility of the dislocation. In this case, the ductility decreases, and the fragility of the material increases. When a metal product containing impurities is under prolonged static stresses, the aging of the sample develops due to the Cottrell atmospheres formation around the dislocations [3]. The speed and tendency to the formation of Cottrell atmospheres are affected by the binding energy of the impurity atom with the dislocation, the migration energy of the impurity atom in the metal, i.e. its diffusion mobility, and the presence and effectiveness of various "traps" for impurity atoms – defects of various types or atoms of other elements (Mn, Cr, etc. [3]) which are introduced, in particular, to prevent aging.

In our work, the molecular dynamics method is used to study the interaction of impurity atoms of carbon, nitrogen, and oxygen with edge dislocations in fcc metals nickel, silver, and aluminum. The binding energies of impurity atoms with edge dislocations and the energy of their migration along dislocation core were calculated. The choice of Ni, Ag, and Al is explained by the unique combination of their properties: two of these three metals have almost identical atomic radii (Ni – 1.24 Å, Ag – 1.44 Å, Al – 1.43 Å [1]), while the other two have almost identical electronegativities (Ni – 1.91, Ag – 1.93, Al – 1.61 [5]), which is indirectly related to the bond strength of metal atoms with impurity atoms.

Earlier in [6], we have already found the binding energies of impurity atoms with edge dislocations in these metals. However, it was found that some of the values were found incorrectly, which, apparently, was due to the insufficient length of the dislocation core in the previously used model. In the present work, in addition to new data on the binding energy, we calculated the migration energies of impurity atoms along the cores of edge dislocations.

2. Creating an edge dislocation in the model

In fcc crystals, the slip system $\{111\}\langle 110\rangle$ is predominant [2,7]. The $\{111\}$ planes are the most closely packed, stacking faults are formed in the same planes. Burgers vector of the perfect dislocation is equal to $1/2\langle 110\rangle$. However perfect dislocation in fcc crystals, as a rule, splits into two partial dislocations with Burgers vectors $1/6\langle 112\rangle$, between which a stacking fault is formed.

The computational cell in the molecular dynamics model had the shape of an elongated parallelepiped (Fig. 1a) and contained about 60,000 atoms. Along the X and Y axes in Fig. 1a, periodic boundary conditions were specified, and along the Z axis – rigid one. Atoms in the border region highlighted blue in Fig. 1a were fixed relative to each other. A similar combination of boundary conditions is often used in modeling slip of single dislocations [3,4,8]. The XY (111) plane, in this case, is the slip plane, and the dislocation is introduced by compressing the upper part of the computational cell and stretching the lower one (shown by numbers 1 and 2 in Fig. 1a) along the Y axis by one interatomic distance. The width of the computational cell along the X axis was set equal to 16 interatomic distances (4.0–4.6 nm depending on the metal). In our previous work [6], a width of 10 interatomic distances was taken, which, as it turned out, is not quite enough to model a dislocation core.

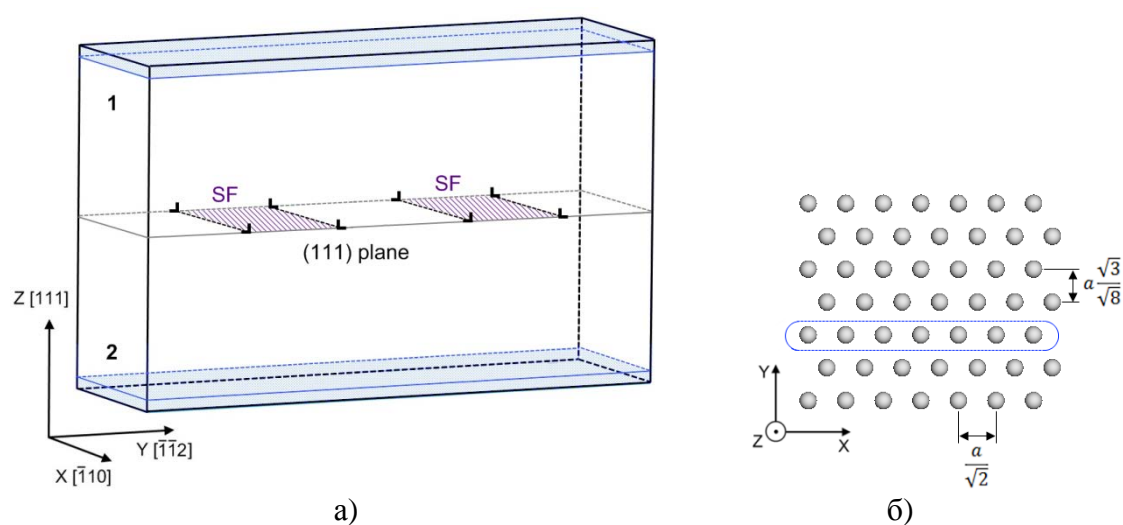


Fig. 1. Modeling edge dislocation in fcc metal: a) model of a complex of two pairs of partial dislocations (SF - stacking fault); b) XY (111) plane with the indication of interatomic distances

Attention should be paid to one important feature of dislocations in fcc crystals. The fact is that the introduction of only one perfect dislocation with Burgers vector $1/2\langle 110 \rangle$ is not enough to maintain the continuity of the crystal on both sides of the slip plane. The fact is that the introduction of only one perfect dislocation is equivalent to the removal or addition of only one atomic half-plane (highlighted in Fig. 1b) oriented along the X axis, which is not enough to preserve the crystal continuity before and after the dislocation. In this case, an additional stacking fault will form even not in the XY (111) plane, but in the other one – $(\bar{1}\bar{1}1)$ (Fig. 2).

Thus, to preserve an ideal crystal before and after a moving dislocation, it is necessary to introduce not one perfect dislocation, but two. More precisely, a complex of two pairs of partial dislocations separated by stacking faults, as in Fig. 1a, which are located in the same plane of {111} type. The sliding speed of such a system is very high and can have values close to the speed of sound in metal.

In the present work, we also considered another type of dislocation – a stair-rod dislocation. An example of a stair-rod dislocation is the edge of a stacking fault tetrahedron – in this case, two half-planes located at a 60° angle relative to each other break off in the dislocation core [7,9]. The second example is grain-boundary dislocations at the tilt boundaries and misfit dislocations at the interphase boundaries between two fcc metals [10,11].

The stair-rod dislocation was created in the model by compressing the upper and stretching the lower parts of the computational cell by one interatomic distance, which corresponds, as was written above, to the introduction of one perfect dislocation. After structural relaxation, an additional stacking fault was formed, oriented in the plane $(\bar{1}\bar{1}1)$ (Fig. 2). The stair-rod dislocation was located along the intersection line of the stacking faults and was stationary, in contrast to the usual dislocation.

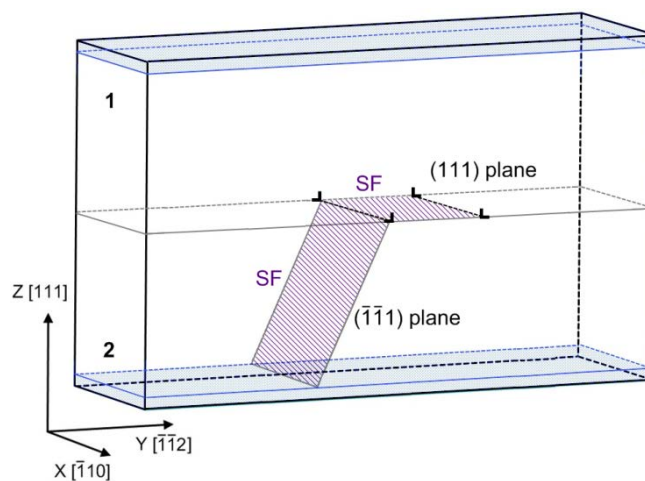


Fig. 2. The stair-rod dislocation

In addition to the dislocations themselves, an important role in the processes associated with diffusion and deformation is played by jogs on them. As noted in [9,10], grain-boundary edge dislocations and misfit dislocations differ from ordinary intragrain dislocations not only in that they are usually stair-rod (or paired) but also in that they contain a high density of jogs (steps). The jogs at the stair-rod dislocations in this work were created by introducing monatomic steps at the edge of the atomic half-plane resulting from the removal of its second part. After this, structural relaxation and following cooling were carried out.

Interactions between metal atoms were described by the many-particle potential of Cleri and Rosato, constructed in the tight-binding approximation [12]. To describe the bonding of Ni, Ag, and Al atoms with C, N, and O impurity atoms, we previously in [13] developed Morse potentials. The parameters of Morse potentials in [13] were calculated taking into account the known characteristics and empirical dependencies for metal-impurity systems, such as the activation energy of diffusion of an impurity atom in a metal crystal lattice, the melting or decomposition temperature of the corresponding interstitial phase, etc. Besides, an additional approbation of the potentials on binding energy with vacancies and dislocations was carried out, which showed good agreement with the results of other authors. Both types of potentials, Morse and Cleri-Rosato, were often used by us earlier in molecular dynamics calculations and have proven themselves well in calculating various characteristics of metal systems and modeling various processes [9-14]. Morse potentials were also used to describe the interaction of impurity atoms with each other, but potentials developed by other authors were taken as a basis for their determination. For the C–C bond, the potential from [15] was transformed into the Morse potential. The potentials for the N–N and O–O bonds were built based on the potentials from [16,17].

3. The binding energy of an impurity atom with an edge dislocation

The binding energy of an impurity atom with a dislocation was calculated as the difference between the potential energies of the computational cells with combined and separated defects. Before calculating the energy, the structure was relaxed with the following cooling to 0 K. In both cases, the position of the impurity atom was chosen such that the potential energy of the computational cell was minimal, i.e. the position of the impurity atom was the most energetically advantageous. The binding energies of impurity atoms with a partial dislocation, a stair-rod dislocation, and also with a jog at a stair-rod dislocation were calculated. The obtained values are shown in Table 1.

Table 1. The binding energy of an impurity atom with an edge dislocation (eV)

| | Ni | | | Ag | | | Al | | |
|--------------------------------|------|------|------|------|------|------|------|------|------|
| | C | N | O | C | N | O | C | N | O |
| Partial dislocation | 0.08 | 0.09 | 0.11 | 0.05 | 0.07 | 0.09 | 0.26 | 0.34 | 0.43 |
| Stair-rod dislocation | 0.77 | 0.72 | 0.62 | 0.30 | 0.25 | 0.22 | 1.14 | 0.88 | 0.44 |
| Jog at a stair-rod dislocation | 0.87 | 0.80 | 0.62 | 0.24 | 0.18 | 0.12 | 0.72 | 0.39 | 0.28 |

Compared with the data presented in [6], the binding energies of impurity atoms with the stair-rod dislocation and the jog on it for Ag and Al are corrected.

According to the data obtained, partial dislocations have a weak interaction with impurity atoms compared with stair-rod ones. Stair-rod dislocations have significantly higher sorption ability with respect to impurity atoms. For comparison, the binding energies of a carbon impurity with dislocations in iron are presented in [4,18]: 0.4–0.7 eV. For oxygen impurities, the binding energy with a dislocation of 0.5 eV was obtained in [19].

The jog at a stair-rod dislocation ambiguously affects the binding energy (last row of the table): for Ni, it is higher than for the undistorted stair-rod dislocation, but for Ag and Al, on the contrary, lower. Ni differs from Ag and Al in that it has a smaller lattice parameter (3.524 Å), while the interatomic distances in Ag and Al are approximately the same (4.086 Å and 4.05 Å, respectively).

It can be seen from Table 1 that the binding energy of an impurity atom with a dislocation is determined mainly by two factors: the depth of the interaction potential of the impurity atom with metal atoms and the ratio of their sizes. For this reason, in most cases, the binding energy for carbon with dislocations was greater than for oxygen atoms.

4. Migration energy of impurity atoms along a partial dislocation

The migration energy of an impurity atom along a partial dislocation was determined by the height of the energy barrier during it moving along the dislocation core. At the first stage, an impurity atom was introduced into the core of a partial dislocation, after which structural relaxation was carried out. Then, the impurity atom was successively shifted a small distance along the dislocation core (along the X axis in Fig. 3). For each position of the impurity atom, a relaxation of the structure was carried out, during which the displaced impurity atom remained stationary and the energy of the computational cell was calculated. The migration energy was determined by the height of the energy barrier of the impurity atom migration. The obtained values are shown in Table 2. For comparison, Table 2 also shows the migration energy of impurity atoms in an ideal crystal lattice.

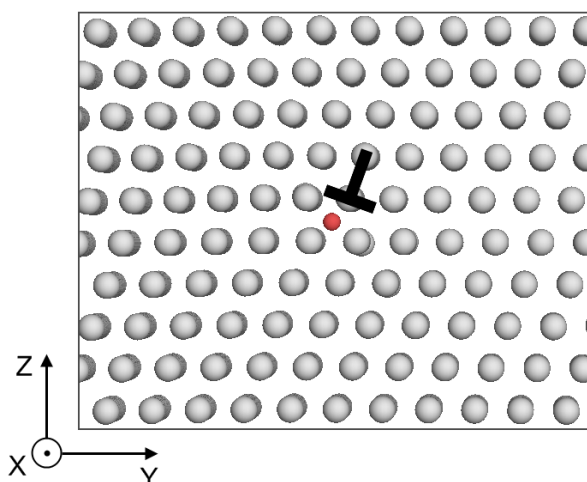


Fig. 3. To the method for determining the migration energy of an impurity atom along a dislocation core

Table 2. Migration energy of an impurity atom along a partial dislocation core (eV)

| | Along a partial dislocation core | | | In an ideal crystal | | |
|----|----------------------------------|------|------|---------------------|------|------|
| | C | N | O | C | N | O |
| Ni | 0.21 | 0.26 | 0.27 | 1.57 | 1.86 | 2.04 |
| Ag | 0.32 | 0.38 | 0.42 | 1.43 | 1.64 | 1.87 |
| Al | 0.38 | 0.39 | 0.44 | 1.34 | 1.51 | 1.76 |

As can be seen from the data obtained, the migration energy of impurity atoms is much lower than the migration energy in a pure crystal, which is consistent with the results of other researchers [18,20-22]. It should also be noted that it is approximately the same for all metals and impurity atoms, slightly increasing from carbon to oxygen and from nickel to aluminum.

Jogs at dislocations play an important role in the processes of self-diffusion or hetero-diffusion of atoms having a relatively close size. In this case, they are, as it were, the weak points where the chains of atomic displacements begin and end during diffusion [23]. However, in the case of diffusion of impurity atoms having a size significantly smaller than the size of metal atoms, the jogs on dislocations obviously act as stoppers that inhibit

diffusion. Therefore, an increase in their density at dislocations should lead to a slowdown in the diffusion of impurity atoms along the dislocation.

5. Conclusion

Using the molecular dynamics method, the binding energies of impurity atoms of light elements C, N, O with edge dislocations, and the energy of their migration along dislocation core in metals with fcc lattice Ni, Ag, and Al were calculated. It is shown that the binding energy with partial dislocations is significantly lower than with stair-rod ones. It was found that the binding energy of an impurity atom with a dislocation is determined mainly by two factors: the depth of the interaction potential of the impurity atom with metal atoms and the ratio of their sizes. For this reason, in most cases, the binding energy for carbon with dislocations was greater than for oxygen atoms.

According to the results obtained, the binding energy with jogs on dislocations turned out to be greater than the binding energy with an undistorted dislocation only for Ni, which has a smaller lattice parameter than Al and Ag.

The values of the activation energy of the impurity atoms diffusion along the dislocation core were found. The obtained values are several times lower than the activation energy of impurity diffusion in a pure crystal. This result indicates a facilitated diffusion of impurity atoms along dislocations compared with diffusion in the crystal volume.

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