The kinetics of point defects in metals under ion irradiation

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Abstract. Modeling an irradiation process of a copper plate for studying the formation and evolution of point defects, that are vacancies and interstitials, is presented in this work. The point defects formation energies were estimated for fcc Cu using molecular dynamics simulation. These values were applied at calculations of atomic concentrations of vacancies and interstitials by numerically decision of kinetic equations. The results of molecular dynamics simulation showed that the interstitial formation energy is more than the vacancy formation energy. These values are in satisfactory agreement with the experimental data. The results of calculations of atomic concentrations of defects confirmed that interstitials are more mobile and their absorption by stocks is more intense.

1. Introduction
Radiations of different types during their interaction with metal violate its periodic structure, and cause an appearance of different types of defects that change mechanical properties of irradiated material. At high doses of irradiation, it can lead to swelling of structural materials.

Primary and secondary processes of the defects formation can be allocated. The primary processes are the development of a cascade of atomic collisions and the formation of point defects, and the secondary processes are migration and association of these defects.

Classical molecular dynamics (MD) techniques are applied in this work to estimate the point defects formation energies. The interatomic potential available for simulation of pure copper is described in an article [1] (EAM1). Calculations of atomic concentrations of vacancies and interstitials are performed by using values of the formation energies. The plate is considered to be infinitely long (the plate width is equal to 1 µm), so a one-axis task is solved. Homogeneous and inhomogeneous cases are studied. Irradiation is pulse-like. The Euler scheme is used to fulfill the homogeneous task, a central-difference scheme is used to solve the inhomogeneous task. The values of the point defects formation energies and concentrations can be used at decision of many tasks of radiation physics.

2. The point defects formation energies
Vacancies and interstitials in fcc Cu were studied in a supercell with \( n = 864 \) atoms \((6a \times 6a \times 6a\) fcc cell size, where \( a \) is a lattice parameter). The point defects formation energies, \( E_{\text{f}}^v \) and \( E_{\text{f}}^i \), were determined as follows [1]:

\[
E_{\text{f}}^v = E_{n-1} - \frac{n - 1}{n} E_n,
\]

(1)
Here \(E_n\) is the energy of this supercell, \(E_{n-1}\) is the energy of the supercell containing a single vacancy, \(E_{n+1}\) is the energy of the supercell containing a single interstitial. The formation energies included in Eq. (1) and Eq. (2) were determined from MD simulation. It was performed at the constant temperature using npt ensemble. The interatomic potential presented in an article [1] is used.

The point defects formation energies obtained from MD simulations at different temperatures (100-900 K) and zero pressure are presented at figure 1.

![Figure 1. The formation energies of interstitials (a) and vacancies (b) as functions of temperature.](image)

These values do not have explicit dependence on temperature \((E_{fi} > E_{fv})\). Similar results were obtained by other investigators for uranium [2]. The formation energies are in satisfactory agreement with the experimental data (see table 1).

|               | Experiment | MD-simulation |
|---------------|------------|---------------|
| \(E_{fv}\), eV [3] | 1.27       | 1.32 ± 0.07   |
| \(E_{fi}\), eV [4] | 2.8–4.2    | 3.15 ± 0.04   |

3. Kinetic equations
The atomic concentration of defects shows a number of defects per one irradiated atom. This value is dimensionless. For a calculation of atomic concentrations of vacancies and interstitials following equations are solved numerically [5]:

\[
\frac{\partial n_v}{\partial t} + \nabla \mathbf{j_v} = G - \alpha (n_v n_i - n_v^{(0)} n_i^{(0)}) - \nu_v P_v (n_v - n_v^{(0)}),
\]
\[ \frac{\partial n_i}{\partial t} + \nabla j_i = G - \alpha(n_v, n_i - n_v^{(0)} n_i^{(0)}) - \nu_i P_i(n_i - n_i^{(0)}). \]  

(4)

Here \( n_{v,i} \) are atomic concentration of vacancies and interstitials, \( n_{v,i}^{(0)} \) are corresponding equilibrium atomic concentration of vacancies and interstitials, \( j_{v,i} = -D_{v,i} \nabla n_{v,i} \) are densities of currents of point defects, \( \nu_{v,i} \) are frequency factors (frequencies of jumps), \( P_{v,i} \) are probabilities of capture of defect by an absorber, \( G \) is a number of defects generated by the source per 1 second, divided to the number of atoms. The function of the source can be determined as follows:

\[ G = \begin{cases} \text{const}, & t < t_0, \\ 0, & t > t_0. \end{cases} \]  

(5)

Here \( t_0 \) is time of an impulse, constant is calculated at condition that a density of a current of ions is equal to 1.

Diffusivities are determined by the following expression [6]:

\[ D_{v,i} = D_0 \exp\left(-\frac{E_{f}^{i} + E_{m}^{v}}{kT}\right), \]

(6)

where \( D_0 = 10^{-6} \text{ m}^2/\text{s} \) [7], \( E_{f}^{i} \) is an energy of formation of a vacancy (see Eq. (1)), \( E_{m}^{v} \) is an energy of formation of an interstitial (see Eq. (2)), \( E_{m}^{v} = 0.72 \text{ eV} \) is an energy of migration of a vacancy [3], \( E_{m}^{i} = 0.117 \text{ eV} \) is an energy of migration of an interstitial, \( T = 300 \text{ K} \) is a temperature of the sample.

Equilibrium atomic concentrations:

\[ n_{v,i}^{(0)} = N_{v,i} \exp(-E_{f}^{i}/kT), \]

(7)

where \( N_{v,i} \approx 5 \).

The coefficient of recombination of point defects [8]:

\[ \alpha = \alpha_v \nu_v + \alpha_i \nu_i \approx \alpha_i \nu_i, \]

(8)

where \( \alpha_i, \alpha_v \approx 1 \) are geometric factors.

Frequencies factors [9]:

\[ \nu_{v,i} = \nu_{v,i}^{(0)} \exp(-E_{m}^{v}/kT), \]

(9)

where \( \nu_{v}^{(0)} = 5 \times 10^{13} \text{ s}^{-1}, \nu_{v}^{(0)} = 10^{13} \text{ s}^{-1} \). The probability of capture of defect by absorber is equal to \( 10^{-7} \). An equilibrium atomic concentration of defects are determined in absence of the irradiation:

\[ n_{v}^{(0)} \approx 2.4 \times 10^{-21}, n_{i}^{(0)} \approx 5.9 \times 10^{-37}. \]

4. Numerically decision

In a homogeneous case \( \nabla j_i = 0, \nabla j_v = 0 \). Equations are solved by the Euler method. Numerical scheme [10]:

\[ n_{v,k}^{i+1} = n_{v,k}^{i} + (G - \alpha(n_{v,k}^{i} n_{v,k}^{i} - n_{v}^{(0)} n_{i}^{(0)}) - \nu_v P_v(n_{v,k}^{i} - n_{v,k}^{(0)}))\Delta t, \]

(10)

\[ n_{i,k}^{i+1} = n_{i,k}^{i} + (G - \alpha(n_{i,k}^{i} n_{i,k}^{i} - n_{v}^{(0)} n_{i}^{(0)}) - \nu_i P_i(n_{i,k}^{i} - n_{i,k}^{(0)}))\Delta t. \]

(11)

Considered times of irradiation \( t_0: 1 \mu \text{s}, 10 \mu \text{s}, 100 \mu \text{s}. \)

A central-difference scheme is used to numerical solving of heterogeneous task [10]:

\[ n_{v,k}^{i+1} = n_{v,k}^{i} + \gamma(n_{v,k-1}^{i} - 2n_{v,k}^{i} + n_{v,k+1}^{i}) + (G - \alpha(n_{v,k}^{i} n_{v,k}^{i} - n_{v}^{(0)} n_{i}^{(0)}) - \nu_v P_v(n_{v,k}^{i} - n_{v,k}^{(0)}))\Delta t, \]

(12)

\[ n_{i,k}^{i+1} = n_{i,k}^{i} + \gamma(n_{i,k+1}^{i} - 2n_{i,k}^{i} + n_{i,k-1}^{i}) + (G - \alpha(n_{i,k}^{i} n_{i,k}^{i} - n_{v}^{(0)} n_{i}^{(0)}) - \nu_i P_i(n_{i,k}^{i} - n_{i,k}^{(0)}))\Delta t, \]

(13)

where \( \gamma = D\Delta t/h^2 \).

Considered times of irradiation \( t_0: 1 \mu \text{s} , 10 \mu \text{s}. \)
5. Analysis of results

During modeling an irradiation process only creation of a Frenkel couple are considered, so that
the same number of defects of both types is appeared in the beginning of the irradiation (in the
homogeneous and heterogeneous cases). Further evolution of defects is determined by following
processes:

1) Mutual recombination

Atomic concentrations of vacancies and interstitials reduce equally by mutual recombination.

2) Absorption of defects by stocks

Extended defects (pore, dislocation) and free boundaries are stocks of point defects. Interstitials have
the smallest energy of migration and, consequently, greater mobility, characterized by the frequency of
the jump \( \nu_i = 10.87 \times 10^{10} \text{ s}^{-1}, \nu_v = 41.14 \text{ s}^{-1} \), therefore
absorption by stocks for them is more intense. Results of calculations of atomic concentrations
of defects before and after the irradiation during 1 \( \mu \text{s} \) for homogeneous case in a logarithmic
scale are presented at figure 2.

![Figure 2](image)

**Figure 2.** Dependence of atomic concentration of interstitials (a) and vacancies (b) on time (s)
under the irradiation during 1 \( \mu \text{s} \) for homogeneous case (in a logarithmic scale).

These values take the maximum value at the end of the pulse (1 \( \mu \text{s} \)):

\[
 n_v^{max} \approx 7.36 \times 10^{-9}, \quad n_i^{max} \approx 7.32 \times 10^{-9}.
\]

A concentration of interstitials reduces fast and tends to an equilibrium value, because their
absorption by stocks is intense. It is equal to \( 10^{-37} \) when time is equal to \( 10^{-2} \text{ s} \). Vacancies are
more sustainable, therefore, their atomic concentration changes little. It is equal to \( 7.31 \times 10^{-10} \)
when time is more than \( 9.8 \times 10^{-4} \text{ s} \). So we can neglect by changing of this value \( dn_v \ll n_v \).
Similar calculations are performed for a longer irradiation.

Spatial distribution of atomic concentrations of defects under the irradiation during 1 \( \mu \text{s} \) for
heterogeneous case at different times are presented at figure 3 (a logarithmic scale is used for
atomic concentrations of defects).

These values take the maximum value at the end of the pulse (1 \( \mu \text{s} \)). A number of defects
reduces and tends to an equilibrium value due to processes of mutual recombination and
absorption by stocks. Domed shape graphs confirm that the boundaries of the sample are stocks
of defects. Equilibrium of flowers of vacancies is achieved at $t = 6.53 \mu s$. Equilibrium of flowers of interstitials is achieved at $t = 10.18 \mu s$, but at $t = 6.53 \mu s$ their atomic concentration is close to an equilibrium value, that is much less than an equilibrium concentration of vacancies. This confirms that interstitials are more mobile than vacancies. Similar calculations are performed for a longer irradiation.

6. Conclusion
The MD-simulation for determination of the point defects formation energies in fcc Cu was performed in this work. These values were obtained at different temperatures (100–900 K) and zero pressure. They agree with the data measured experimentally.

Atomic concentrations of vacancies and interstitials in a plate of copper were obtained by using the calculated formation energies. Interstitials are more mobile than vacancies and their absorption by stocks is more intense, so that their atomic concentration reduces fast and tends to an equilibrium value. Atomic concentration of vacancies changes a little. It is equal to $7.31 \times 10^{-10}$ when time is more than $9.8 \times 10^{-4}$ s (in homogeneous task). This can explain swelling of material.

Receipt of the point defects migration energies and diffusivities using molecular dynamics simulation can be a continuation of work.

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