Computer Simulation of Formation Energy and Migration Energy of Vacancies under High Strain in Cu^{*1}

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Recently it has been reported that many vacancy clusters are generated at sawtooth-like fractured tips of thin foils. The elastic strain of the torn portion is more than 10% before the fracture, which is expected to cause the generation of many vacancy clusters. In this paper, the formation and migration behaviors of vacancies in Cu under high elastic strain from 10% compression to 20% elongation were studied by computer simulation using the effective medium theory (EMT) potential. The model lattice was elastically deformed along the $\langle 110 \rangle$ and $\langle 100 \rangle$ directions. Poisson's ratio was determined to minimize the total energy. After full relaxation of the lattice by the static method (Newton-Raphson method) under fixed boundary conditions, a vacancy was introduced and the change of the total energy (formation energy) was calculated. The migration energy of vacancies was obtained as the total energy difference between the model lattice with an atom at the lattice point and the atom at the saddle point. High strain dependence of these energies is obtained. For example, the formation and the migration energies of vacancies are 1.21 eV and 0.79 eV in the absence of deformation, respectively. The formation energy in the $\langle 100 \rangle$ deformation is 1.09 eV and 1.13 eV by 10% compression and 10% elongation, respectively. The migration energies and the migration distances vary with the migration direction. For example, the migration energy for the shortest migration distance in the $\langle 100 \rangle$ deformation is reduced to 0.45 eV and 0.26 eV by 10% compression and 10% elongation, respectively. While that for the longest migration distance increases to 1.29 eV by 10% compression. These results are explained by the configuration of neighboring atoms nearest to the vacancy.

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1. Introduction

Kiritani *et al.*¹⁻⁵⁾ have reported a generation of many vacancy clusters at fractured tips of thin foils of fcc metals. Immediately before the fracture, they also observed that the elastic strain of the sawtooth-like torn portion is more than 10% in Au, Cu and Ni by electron microscopy diffraction analysis.

In previous studies, in order to understand point defect processes under high strain, calculations for the formation and the migration energies of vacancies under high strain of the $\langle 110 \rangle$ direction were reported.^{6,7)} In these calculations, however, there are two deficiencies. One is the employment of the Finnis-Sinclare (FS) potential, which is not suitable for calculations under high strain. In this study, we have employed the effective medium theory (EMT) potential, because the stress-strain curve for the EMT potential is similar to that by a first-principle calculation under high elastic strain. The other deficiency is the usage of the experimental value of Poisson's ratio (Cu: 0.343) even at a high strain of 10%. In this study, we used fixed boundary condition in our model lattice fixing Poisson's ratio, which was predetermined to minimize the total energy of the model lattice, and both the formation and the migration energies of vacancies under high strain along the $\langle 110 \rangle$ direction as well as the $\langle 100 \rangle$ direction were calculated. The choice of the $\langle 100 \rangle$ direction is due to the fact that Matsukawa *et al.* observed the strain of more than 10% using [200] diffraction spots.^{4,5)}

2. FS and EMT Potentials

Both the FS and the EMT potentials are many-body potentials for metallic systems. The electron density of the sample is allowed to vary from one lattice site to another. The main part of the cohesion at a given lattice site depends on the local electron density at this site. The total energy of the system composed of N atoms can be written as

$$E_{tot} = \sum_{i=1}^N F(n_i) + \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N V(r_{ij}), \quad (1)$$

where $V(r_{ij})$ is a pair potential, n_i is a quantity describing the local density at the atomic site i and $F(n_i)$ is the corresponding energy term. The local density n_i is dependent on the distances from the atom i to its neighbours. In this way, $F(n_i)$ is structure dependent and implicitly includes many-atom interactions.⁸⁻¹¹⁾

The FS potential has been called a semi-empirical potential. Thus, the parameters have been fitted to experimental values. In the previous papers,^{6,7)} we used parameters obtained by Ackland *et al.* for Cu,¹⁰⁾ which were fitted to the lattice constants a , the cohesive energy E_c , the elastic constants C_{11} , C_{12} and C_{44} , the vacancy formation energy E_v^f and the stacking fault energy. On the other hand, the EMT potential has been generally known as a non-empirical potential, which is constructed on the basis of the first-principle theory without any experimental data.¹¹⁾ While the semi-empirical EMT potential has been also developed. We used the parameters obtained by Jacobsen *et al.* for Cu,¹²⁾ which were fitted to the cohesive energy, the lattice constants and the elastic constants.

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Fig. 1 The size and orientation of the model lattice (' a ' denotes atomic distance). (a) and (b) were elastically deformed along the $[\bar{1}10]$ direction and the $[100]$ direction, respectively.

3. Method of Calculation

Figures 1(a) and (b) show the size and orientation of the model lattice we employed. The lattice in Figs. 1(a) and (b) was deformed along the $[\bar{1}10]$ (x_a) direction and the $[100]$ (x_b) direction, respectively. The model lattice in Fig. 1(a) was shrunk in both the $[111]$ (y_a) direction and the $[\bar{1}12]$ (z_a) direction in response to tensile deformation and expanded in the same directions in response to compressive deformation, in accordance with Poisson's ratio, respectively. The model lattice in Fig. 1(b) was also deformed in the $[010]$ (y_b) direction and the $[001]$ (z_b) direction in the same way. For comparison we used two Poisson's ratios; one was the experimental value: 0.343 and the other was the value which minimized the total energy of the deformed model lattice. The value of Poisson's ratio calculated with the EMT potential which minimizes the total energy is shown in Fig. 2. As we only had an interest in elastic deformation, we did not

Fig. 2 Strain dependence of calculated Poisson's ratio in Cu optimized by the EMT potential. The ν_{y_a} and ν_{z_a} are Poisson's ratios in the $\langle 110 \rangle$ deformation, the ν_{y_b} and ν_{z_b} in the $\langle 100 \rangle$ deformation. Square mark denotes the experimental value: 0.343. The plus and minus signs indicate tensile and compressive strain, respectively.

introduce dislocations even if the stress of the model lattice exceeded the yield stress. Subsequently, the lattice was fully relaxed by the static method (Newton-Raphson method) under fixed boundary conditions, where 5 layers from the surface were fixed. This static method corresponded to an energy calculation at 0 K. The possibly largest size of the model lattice was chosen in order to avoid the boundary effect.

The vacancy formation energy under deformation was determined according to the following processes. First, we deformed and relaxed the model lattice, and calculated the total energy (Total energy 1). Next, we introduced a vacancy into the relaxed model lattice by removing one atom from the center of the lattice composed of N atoms, and calculated the total energy after full relaxation (Total energy 2). The vacancy formation energy was obtained as the difference between Total energy 1 of a lattice composed of $N-1$ atoms and Total energy 2 of a lattice composed of $N-1$ atoms and a vacancy.

The migration energy was given by the difference between the total energy of the model lattice with an atom before the migration and with the atom at a saddle point. The migration of a vacancy from position (A) to (B) in Fig. 3 is equivalent to the migration of the atom from position (B) to (C) and (A). At the saddle point, the atom is at position (C), where the total energy of the model lattice is at its maximum along the particular migration path. The atom was fixed at position (C) and the other atoms were fully relaxed.

4. Results and Discussion

4.1 Stress-strain curve for FS and EMT potentials

It is impossible to obtain the stress-strain curve under high elastic strain by experiments because dislocations are introduced in metals. Therefore, the stress-strain curve by first-principle calculation is the only one we can obtain without the introduction of dislocations. Stress-strain curves, where Poisson's ratio is zero and the strain is along the $\langle 100 \rangle$ direction in Al and Cu, are shown in Figs. 4(a) and (b), respectively. Those curves obtained by the first-principle calculation and the EMT potential in Al have been reported in Refs. 13) and 14), and others were obtained in this study.

Two curves by the first-principle and the EMT calculations for Al are very similar. On the other hand, our calculation

Fig. 3 The migration of a vacancy. (A) is a vacancy site, (B) is the first nearest-neighbor atom that will migrate to the vacancy site, and (C) is the saddle point. Dotted circles and solid circles are the atomic position before and after the relaxation, respectively.

Fig. 4 The stress-strain curve under tensile strain in (a) Al and (b) Cu. *Ab initio*, EMT, FS and FS* are results by a first-principle calculation,^{13,14} calculations with the EMT potential,^{13,14} the FS potential and the FS potential without summation of the pair potential term of the second nearest-neighbor atoms, respectively.

with the FS potential fitted by Vitek *et al.*^{15,16} was different from the result by the first-principle calculation when the strain is above 5%. The maximum and minimum values of the stress appeared at $\varepsilon \approx 10\%$ in the calculation with the FS potential are unnatural. This deficiency was caused by the pair potential term shown in Fig. 5. The pair potential term had the maximum at $r/r_0 \approx 1.09$ (Al) and ≈ 1.08 (Cu). Namely, the first derivative of the pair potential term changed from positive to negative values there. The change in the first derivative of the pair potential term brought negative contribution to the total stress, when the distance from the second nearest-neighbor atoms got to this range by elongation. This is because the stress-strain curves for many-body potentials were evaluated by,

$$\sigma_{ij} = \frac{1}{V} \frac{\partial E}{\partial \varepsilon_{ij}}$$

Fig. 5 The pair potential term of the FS potential in Cu and Al against normalized distance (r_0 : lattice constant).

$$= \frac{1}{2V} \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{\partial E}{\partial r_{\alpha\beta}} \frac{r_i^{\alpha\beta} r_j^{\alpha\beta}}{r^{\alpha\beta}}, \quad (2)$$

where V is the total volume of the model lattice.¹⁷ If we fit the parameters of the FS potential to the experimental values obtained under high elastic strain, the maximum and the minimum of the stress may disappear. As we cannot obtain these values at this time, the EMT potential is thought suitable for calculations under high elastic strain in Al.

There are no stress-strain curves by the first-principle calculation for Cu. The shapes of the stress-strain curves in Al and Cu were very similar in each potential. Therefore, only the calculation with the EMT potential is shown in the following sections.

In this calculation with the EMT potential, the formation and the migration energies of vacancies in the absence of deformation were obtained as 1.21 eV and 0.79 eV, which were nearly equal to the experimental values: 1.28 ± 0.05 eV and 0.70 ± 0.02 eV, respectively.¹⁸

4.2 Effect of Poisson's ratio on the total energy

In our model calculation, as the boundary condition was fixed, Poisson's ratio was changed as a parameter. As shown in Fig. 6, the vacancy formation energy with the calculated Poisson's ratio which minimize the total energy in the $\langle 110 \rangle$ deformation was different from the energy calculated with the experimental Poisson's ratio: 0.343. The positive and negative values indicate tensile and compressive strain, respectively. Discrepancy between the vacancy formation energies with the experimental Poisson's ratio and the calculated one increased with increasing the strain. The calculation shows the lattice with the calculated Poisson's ratio is more stable, because the total energy of the model lattice was minimized. The vacancy formation energy with the calculated Poisson's ratio was higher than the one with the experimental Poisson's ratio. These results indicate that the introduction of a vacancy into the stable deformed lattice requires higher energy.

Fig. 6 Variation in vacancy formation energy with strain. The energies are calculated with the experimental value of Poisson's ratio: 0.343, and values calculated to minimize the total energy in the $\langle 110 \rangle$ deformation.

Fig. 7 Variation in vacancy migration energy with strain. The energies are calculated with the experimental value of Poisson's ratio: 0.343, and values calculated to minimize the total energy in the $\langle 110 \rangle$ deformation.

Figure 7 shows the variation in the vacancy migration energy calculated with the experimental Poisson's ratio and the calculated one in the $\langle 110 \rangle$ deformation. The discrepancy between the vacancy migration energies with the experimental Poisson's ratio and the calculated one increased with increasing the strain. Under high strain, the change in Poisson's ratio had a great influence on both the formation and the migration energies of vacancies. Only the result calculated with the calculated Poisson's ratio is shown in the following sections.

4.3 Vacancy formation energy

Figure 8 shows the variation in the vacancy formation energy in Cu by the $\langle 110 \rangle$ deformation and the $\langle 100 \rangle$ deformation. In 20% tensile strain along the $\langle 100 \rangle$ direction, we could not determine the formation energy of vacancies owing to the instability of the model lattice. With increasing the compressive strain, the vacancy formation energy decreased. When the tensile strain increased, the vacancy formation energy was constant below 5% strain, and then decreased.

When the tensile strain increased, an average volume per one atom also increased. The volume was determined by dividing the total volume of the model lattice into the number of atoms. The volume of a vacancy given by the third power

Fig. 8 Variation in vacancy formation energy with strain in Cu along the $\langle 110 \rangle$ deformation and the $\langle 100 \rangle$ deformation.

of the average distance from the vacancy site to the twelve nearest-neighbor atoms, however, was not proportional to the average atomic volume. For the $[100]$ deformation, the vacancy formation energy decreased and the ratio of the vacancy volume to the average atomic volume also decreased with increasing the tensile strain. But, for the $\bar{1}10$ deformation, the ratio was almost constant. The variation in the vacancy formation energy for the $\bar{1}10$ tensile deformation is explained as follows. The energy change of neighboring atoms which are nearest to the vacancy before and after the introduction of a vacancy increased with increasing the tensile strain. However, the energy of other neighboring atoms decreased. When each energy change was summed, the total change decreased. Consequently the vacancy formation energy decreased with the increase of the tensile strain. In the present calculation, the change in the vacancy formation energy was explained only by the energy change of atoms near the vacancy.

4.4 Vacancy migration energy

The migration energy of vacancies changed along with migration direction. In the case of the $\bar{1}10$ deformation, as shown in Fig. 9(a) for tensile deformation, the migration distance was longest along the $\bar{1}10$ direction, and shortest along the $[110]$ direction. The relation was opposite in the case of compressive deformation (Fig. 9(b)). The distance between the vacancy and one of the eight nearest-neighbor atoms is between the values of the longest and the shortest distances mentioned above. These migration distances can be classified as "long", "short", and "medium", respectively. In the case of the $[100]$ deformation, the $[10\bar{1}]$ migration direction and the $[0\bar{1}1]$ migration direction can be classified as "long" and "short" in the same way. The migration energies are shown in Fig. 10 for the $\langle 110 \rangle$ deformation and Fig. 11 for the $\langle 100 \rangle$ deformation. For the $\langle 110 \rangle$ deformation, the migration energy for the "short" distance decreased with increasing the strain. When the tensile strain increased, the migration energy for the "medium" distance decreased. The migration energy for the "long" distance, however, increased. On the other hand, for the $\langle 100 \rangle$ deformation, the migration energy for the "short" distance remarkably decreased with increasing the strain. The migration energy for the "long" distance also decreased with increasing the tensile strain, and it increased with increasing the compressive strain.

Fig. 9 The distance between a vacancy and the first nearest-neighbor atoms in (a) the tensile deformation and (b) the compressive deformation (deformation direction: $[1\bar{1}0]$). Dotted circles and solid circles are the atomic position before and after the relaxation, respectively.

Fig. 10 Variation in vacancy migration energy with strain in Cu along the $\langle 110 \rangle$ deformation.

Fig. 11 Variation in vacancy migration energy with strain in Cu along the $\langle 100 \rangle$ deformation.

Fig. 12 A vacancy and the five nearest-neighbor atoms. Distance from position (C) to the window atoms is defined as d .

The migration energy depended on the distance between the moving atom and the surrounding atoms at the saddle point. Figure 12 shows a vacancy and its five nearest-neighbor atoms. When an atom migrates from position (B) to (A), other four nearest-neighbor atoms make a window. The distance from position (C) to the window atoms is defined here as d . If the distance d is long, the atom migrates easily. For example, in the case of 10% tensile strain for the $\langle 110 \rangle$ direction as shown in Fig. 10, the average distance d for the “medium” distance was the longest (giving the lowest migration energy), and the d for the “short” distance the second longest, and the d for the “long” distance the shortest (giving the highest migration energy). But, the difference of the total energy of the five nearest-neighbor atoms between the initial and the saddle point configurations did not depend only on the average distance d . For example, in the case of 10% tensile strain for the $\langle 110 \rangle$ direction, the difference for the “short”, “medium”, and “long” distances contributed to about 100%, 50% and 40% of the migration energy, respectively.

5. Concluding Remark

Both the formation and the migration energies of vacancies under high tensile and compressive strain were calculated for Cu by the semi-empirical EMT potential with Poisson’s ratio which minimizes the total energy. Extremely high strain dependence of these energies was observed. These results suggest that easy formation and fast migration of vacancies under high elastic strain are one of mechanisms for the production of a large number of vacancy clusters observed experimentally at the sawtooth-like fractured tips of thin foils.

Though the present simulation was carried out under uniaxial deformation, the results strongly suggest the existence of easy formation and fast migration of vacancies near defects such as dislocations and precipitates, where high strain regions are expected to exist. The behaviors of point defect near these defects will be discussed in a next paper.

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