Grain boundary sliding and migration in copper: the effect of vacancies

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Abstract

The atomic structure and mechanism of the interface sliding of the \( \Sigma = 5(210)[001] \) symmetric tilt grain boundary (GB) in copper and its interaction with vacancies at an elevated temperature has been studied using a computationally efficient potential based on the Embedding Atom Method in connection with the finite temperature Monte Carlo technique. Grain boundary sliding is performed for pure copper as well as copper containing a vacancy at a selected position. The discontinuous changes of the GB energy at certain sliding distances are associated with GB migrations. Elevated temperature reduces the grain boundary sliding/migration energy by a factor of about 2 but does not increase the rate of migration. Migration of the GB is mediated by the flow of atoms along the interface in coordination with the atoms in bulk. The sliding and migration properties partially depend on the position of the vacancy in the GB core. We found that the grain boundary sliding energy profile in the presence of a vacancy placed at the interface increased the GB energy, but reduces the sliding energy. The sliding process invokes the interface migration in such a way that the vacancy effectively migrates to a more convenient position and reduces the GB energy.

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1. Introduction

Grain boundary sliding (GBS), i.e., the rigid translation of one grain over another parallel to the boundary interface, is one of the principal mechanisms of plastic flow of polycrystalline
materials at intermediate-to-high temperatures [1,2]. The grain boundary migration in the direction perpendicular to the boundary plane may occur during the GBS [3] but interaction between the grain boundary and other defects in the crystal such as vacancies or dislocations should affect the GB migration [4]. Despite the important role of GB in this process, our knowledge of how boundaries actually move at the microscopic level is limited. The advent of fast computers gives a chance to provide an atomic-level insight into GB structure. Simulation at the atomic level in combination with Monte Carlo (MC) technique [5] allows investigating the role of temperature in the migration process [6]. Although the structure and properties for a number of metals can be calculated by ab initio methods [7–9] or by Hartree–Fock calculation [10], computational limitations still prevent such methods from being applied to atomic simulation at elevated temperature. Methods based on fitting parameters such as the Embedded Atom Method (EAM) [11] could be more suitable for this purpose. It has been shown for a number of fcc metals that the EAM technique gives excellent agreement with both ab initio and experimental results [12]. In combination with MC technique it could give progress in atomistic simulations of fcc metals at elevated temperature.

In our previous paper [4], we addressed the mechanism characterizing the sliding process at the $\Sigma 5$ tilt GB in aluminum. We also evaluated the effect of elevated temperature on GB migration rate. For this we carried out MC simulations using EAM potential constructed by Mishin et al. [13]. We find that simulated annealing based on MC technique allows the system to be gradually annealed to a global-minimum configuration, thus increasing the number of migrations and reducing the GB sliding energy barrier by a factor of about three compared to the corresponding zero temperature values. We now contrast these results with the study of the microscopic processes that occur during the sliding of copper grains.

Copper was chosen here because special copper alloys as CuCrZr (98.95wt.%Cu; 0.6–0.9wt.%Cr; 0.07–0.15wt.%Zr) and CuAl25 (99.5wt.%Cu; 0.25wt.%Al as Al$_2$O$_3$; 0.22wt.%O as Al$_2$O$_3$; 0.025wt.%B as B$_2$O$_3$) were selected and as good candidates for heat sinks in the design of International Thermonuclear Experimental Reactor (ITER) Plasma Facing Components [14]. However, impurities can influence the quality of pure copper, their presence (lower than 1% in total) was omitted in our calculations. The main function of the heat sink is to transport elevated heat fluxes to the cooling water, thus reducing thermal stress in the structural material. High heat loading might invoke mechanical or structural changes in the sink material.

The goal of the present work is to investigate the effect of temperature and vacancy on polycrystalline copper. In order to achieve this, we have studied the structure and sliding energy of a $\Sigma 5$ [001] (210) tilt GB in copper in the absence or presence of vacancies at an elevated temperature. The remainder of this paper is organized as follows. Some computational details as the quality of relaxation process and EAM potential used in atomic simulations are discussed in Section 2. In Section 3, we discuss the equilibrium structure and energy of a perfect as well as vacancy containing interface in copper. In Section 4, using equilibrium GB structures computed in previous section, sliding and interface migration is examined under lateral force condition. In Section 5, a brief summary and statement of conclusions are presented.

2. Methodology

2.1. Structural optimization

Our calculations are performed in the framework of a $\Sigma 5$ tilt GB connecting the two copper surfaces of a plate. The boundary was obtained by rotating two perfect copper crystals with (001) face by an angle of 53.13° with respect to each other about the interface. The lattice constant was set to the experimental value of 3.62 Å [16]. The computational configuration of 160 copper atoms is shown in Fig. 1. The closed and open circles represent atoms distributed on the first and second (001) planes. For simulation we used 27 supercells with total number of 4320 copper atoms in combination with Born-von Karman periodic border conditions normal to the interface as well
as parallel to the interface. The obvious disadvantage of such border conditions is that the computational supercell contains two interfaces. This doubles the number of atoms that we wish to consider and may introduce interference between the parallel GBs. Therefore, the care must be taken on the distance between adjacent interfaces along the direction normal (direction (210) in this work) to the GB plane. The computational supercell of 40 (210) atomic layers corresponding to a separation of 16.49 Å between the two GB planes has been found large enough to remove the size effect.

The GB energy was determined from the difference between the energy of a supercell containing the grain boundary and the energy of a supercell containing an equal number of atoms in the bulk environment, divided by the total grain boundary area. The geometry optimization has been made by simulating annealing (SA) technique introduced by Kirkpatrick et al. [18]. It has been shown that if the temperature is reduced slowly enough, conventional SA technique can in principle find the global minimum of energy. In our simulation we started from the initial temperature of 1250 K and the system was cooled to 27 K using a stepwise-exponential decrease of temperature involving a total $350 \times 10^3$ steps. In Fig. 2, we plot the grain boundary energy as a function of the Monte Carlo annealing temperature. The amplitude of the atomic displacements is allowed to vary so that the acceptance rate remains about 0.5 during MC simulations. These amplitudes are typically from 0.02 Å ($T = 1250$ K) to 0.002 Å ($T = 27$ K). The extrapolated zero-temperature GB energy is $0.946 \text{ J/m}^2$. The accuracy of the least-squares fit of the extrapolated zero-temperature GB energy is $7.32 \times 10^{-3} \text{ J/m}^2$.

2.2. Interatomic potential

The EAM potential, if properly designed, gives a good description of metallic materials, in which an important contribution to the interatomic interaction comes from the interactions of the atomic cores with the conduction electrons. The spirit of these potentials is that each atom in a solid is viewed as an impurity embedded in a host comprising all the other atoms. The energy for an $n$-atom system then should be written as

$$E = \sum_{i=1}^{n} E_i,$$

where the energy of single $i$th atom is given by

$$E_i = \frac{1}{2} \sum_{j \neq i} \Phi(r_{ij}) + F(r_i).$$
Here $r_{ij}$ is the scalar distance between atoms $i$ and $j$, $\Phi(r_{ij})$ is a pairwise interaction potential, and $\rho_i$ is the density at $i$th atomic site due to all neighbors (located within a sphere of radius $r_{\text{cutoff}}$)

$$\rho_i = \sum_{j \neq i} \rho(r_{ij}).$$

(3)

The embedding function $F(\rho)$ can be interpreted as the energy arising from embedding $i$th atom in an electron gas of density $\rho_i$. The accuracy of computed results mainly depends on the quality of the embedding function and its ability to treat electron density deviations in local coordination. Therefore we present evidence that the used EAM potential describes a variety of copper properties. In particular we address the bulk. In Table 1 we list the data computed using the EAM potential in comparison with the values predicted by ab initio method and experiment.

### 2.3. Simulation of grain boundary sliding

The grain boundary sliding is simulated quasi-statically, by rigidly shifting the top grain with respect to the bottom by a small specified amount along the [1 2 0] direction. The sliding distance is described in percentage of $a_{\text{CLS}}$, where $a_{\text{CLS}}$ is the lattice parameter of the Coincident Site Lattice (CSL) cell along [1 2 0] direction. The increment $\Delta a = 0.125$ Å (or 1.546% of $a_{\text{CLS}}$) seems to be small enough to capture all the energy jumps. At each displacement the system is then relaxed using MC simulations. In contrast to previous simulations, the MC simulations allow the system to gradually anneal to a global-minimum configuration by lowering the system temperature in successive steps for each displacement. In order to investigate the effect of annealing on the GB sliding properties, namely the energy barriers and the shear displacement at which the GB migration occurs, we have carried out two sets of MC simulations. In both calculations the MC simulated annealing technique proceeds by lowering the temperature from 540 to 27 K. However, in the first, which we will refer to as “static”, the probability acceptance of any higher-energy configuration is set equal to zero, driving the system to the local-minimum configuration. In the second set simulations, the probability acceptance follows the standard MC rules.

### 3. Grain boundary equilibrium structure and energy

The final equilibrium structure of computed GB using SA method shows that the displacements away from the starting structure are small. Most of the atomic movement occurs near the GB plane. In Fig. 3a is shown the relative variation (strain) of the interlayer spacing as a function of the layer away from the GB plane. The strain has an oscillatory profile. Although an atom in a regular fcc structure has 12 nearest neighbors, the number of first-neighbors bonds across the interface is reduced. This in fact invokes a local electron density different from the electron density in the bulk. In Fig. 3b is shown the distribution of energy associated with atoms as a function of the distance from the GB plane. The strain has an oscillatory profile. Although an atom in a regular fcc structure has 12 nearest neighbors, the number of first-neighbors bonds across the interface is reduced. This in fact invokes a local electron density different from the electron density in the bulk. In the second set simulations, the probability acceptance follows the standard MC rules.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Structure and elastic properties of fcc copper computed by the EAM potential in comparison with the values computed by ab initio technique as well as experimentally observed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>Lattice constant (Å)</td>
<td>3.615</td>
</tr>
<tr>
<td>Cohesive energy (eV)</td>
<td>$-3.49$</td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>137</td>
</tr>
<tr>
<td>$C^\prime$ (GPa)</td>
<td>23.7</td>
</tr>
<tr>
<td>$c_{44}$ (GPa)</td>
<td>73.1</td>
</tr>
<tr>
<td>$\Delta(E_{\text{bcc}} - E_{\text{fcc}})$ (meV)</td>
<td>42.7</td>
</tr>
<tr>
<td>$\Delta(E_{\text{hcc}} - E_{\text{fcc}})$ (meV)</td>
<td>444.8</td>
</tr>
<tr>
<td>Stacking fault energy (mJ/m$^2$)</td>
<td>39.5</td>
</tr>
<tr>
<td>Vacancy: $E_f$ (eV)</td>
<td>1.21</td>
</tr>
</tbody>
</table>

$^a$ Ref. [15].

$^b$ Ref. [16].

$^c$ Ref. [19].

$^d$ Ref. [17].

$^e$ Ref. [20].

$^f$ Ref. [21].
The GB properties may be dramatically altered if the vacancy is formed either into the interface core or at the selected site close to the boundary. To study this effect we removed an atom at a selected site in the initial cluster and then allowed the entire structure to relax using the described method of thermal annealing. The relaxed structure then has been examined to determine the vacancy formation energy $E_v$ as function of position. In Fig. 4 is shown $E_v$ versus perpendicular distance from the GB. The change of $E_v$ with the distance is well observable. A deep minimum in the vacancy formation energy ($E_v = 0.22 \text{ eV}$) corresponds to the vacancy created in the first layer from the interface. Another minimum ($E_v = 0.69 \text{ eV}$) is related to the vacancy in the fourth layer from the interface. The low formation energy indicates that the lattice close to the GB (volume between the first and fourth layer) is more heavily populated by defects than the rest of the crystal. A relatively low vacancy formation energy ($E_v = 1.23 \text{ eV}$) was found for the vacancy placed in the GB core. For a vacancy formed in a large distance from GB, $E_v$ is the same as the vacancy formation energy in the bulk ($E_{v, \text{bulk}} = 1.21 \text{ eV}$—computed value).

4. Grain boundary sliding and migration

In Fig. 5 we show the relative variation of the GB energy (with respect to its value for zero displacement) as a function of the grain displacement relative to the lattice parameter of the coincidence lattice cell, ($a_{\text{CLS}}$), for both the “static” (circles) and simulated annealing (triangles) calculations. In both cases the energy profile is smooth, exhibiting several peaks and energy valleys between them, the latter being associated with grain boundary migration. The effect of simulated annealing is to reduce the energy barrier by a factor of about two compared to the corresponding “static” values but, in contrast to simulations on aluminum, sliding by $a_{\text{CLS}}$ does it not increase the number of migrations. The migrations in the simulated annealing simulations occur earlier, for example, the first migration occurs when the shear displacement is about 10% compared to the corresponding
value of 15% in the “static” calculation. Moreover, the simulated annealing simulation gives a shallow minimum on the energy profile after displacement of about 3.72% CSL along the interface and gives the grain boundary energy of 0.966 J/m² at an elevated temperature of 27 K.

The situation is obviously more complicated if a vacancy is formed close to the GB. In order to examine the variation of $E_{\text{GB}}$ during lateral sliding in the presence of a vacancy at a specific position we performed a series of GBS experiments using a defect structure. For relaxation we employed, as before, SA technique using $T_a = 850$ K. The final temperature was 27 K. Positions of vacancies are shown in Fig. 6. Associated GB energy profiles for designed vacancy positions are plotted in Fig. 7. Note, for this simulation we used the increment $\Delta a = 0.25$ Å (or 3.092% of Coincident Site Lattice (CSL) scale). As before, the lateral shift is associated with the GB migration. A surprisingly large change in energy was indicated for GBS containing a vacancy at the GB core (A position in Fig. 6). Such a long jump in the energy profile is always accompanied by defect migration from the sites that cannot support a stable position to the site with a stable configuration. In Fig. 8 we display the atomic configurations associated with some positions during the lateral shift of the structure. Microscopic knowledge of the actual atomic configuration shows that the vacancy, originally placed in the GB plane (Fig. 8a), is transformed through a heavily perturbed configuration (Fig. 8b) to the stable position in the first plane (Fig. 8c). This indicates that vacancy position at the core is not separated (or weakly separated) by a potential barrier from the position at the first layer. In the process of transformation the interface migrates in such a way that the vacancy is replaced in the first plane without real vacancy...
migration. This effect we will refer to as relative vacancy migration. The result is in contrast to our previous computations on GB in aluminum, where it has been shown that a vacancy in the GB core could not be transformed in another configuration. After this transformation next jumps in energy are associated with GB and vacancy migration. On the other hand, the grain boundary sliding with the vacancy formed at the first plane does not affect the relaxation of atoms which are pivotal for the migration. The associated GB energy is very similar to that of the clean GB and is accompanied by interface and vacancy migration.

5. Conclusions

We have studied the interaction between vacancies and the Σ5 tilt grain boundary in copper, using MC calculations in combination with the EAM potential to simulate the sliding and migration of GB at elevated temperature. It has been found that the SA approach reduces the GB sliding energy barrier by a factor of about 2 but the interface mobility is not sensitive to the elevated temperature. This is in reasonable agreement with the recent molecular dynamics results showing the fact that the critical stress necessary to move the GB damps almost exponentially with the temperature [22]. We find that while most of the GB sites have lower vacancy formation energy compared to bulk, those at the interface have higher formation energy. It confirms that certain GB sites do not support vacancy [23]. If the vacancy is formed in such a site it is not able to follow the migrating interface and is refilled by one atom from the site with low vacancy formation energy. This in fact creates a vacancy in the first layer from the interface and invokes the effect of relative vacancy migration. The resulting effect reduces the boundary energy and stabilizes the atomic structure close to the interface.

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References