Grain boundary sliding and migration in copper: A systematic study of vacancy effect

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Abstract

We present a comprehensive study of interaction between the vacancy and Σ5 grain boundary (GB) in copper. 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. The calculations have been done in the framework of the Embedded Atom Method (EAM) potential in the combination with Monte Carlo technique and the local-density approximation (LDA) in the density-functional formalism. The study showed good agreement between EAM and LDA techniques.

I. Introduction

Materials driven far from equilibrium by irradiation [1] are an important element of a prototype fusion power station [2,3]. By studying how the quality of the material varies as a function of radiation dose it is necessary to understand the details of interaction between the radiation defects and the material microscopic structure. While there have been extensive theoretical studies aimed at either vacancies or GBs individually, much less effort has been devoted to the understanding of the collective behavior of GB and vacancies [4,5]. The copper alloys, especially the best candidate for ITER technology CuCrZr, consist of about 99% Cu. Simulations of the GB sliding and migration in pure copper gives a good change to study the effect of radiation defects on structural properties in well defined conditions.

Grain boundaries being an important component of the microstructure of a polycrystalline material are responsible for the various material properties [6,7]. The GB creation in single crystal significantly alters the electron density in the outermost layers [8]. Thus, the neighbor atoms change their atomic positions due to the forces generated by the redistribution of the electron density. The atomic layers shifting perpendicular (inward or outward) to the interface give rise to a change of the interlayer spacing. The determination of the atomic structure is among the basic questions in GB science because the properties are of the grain boundary is largely determined by the atomic-scale structure in the interface region [9].

Grain boundary sliding (GBS), i.e. the rigid translation of one grain over another parallel to the GB interface is the principal mechanism of plastic flow of

polycrystalline materials. The sliding has been extensively studied for decades using variety of experimental and theoretical methods [10]. The mechanism of GBS and its interaction with point defects is of practical importance for developing models of mechanical behavior in metals under radiation [11]. Despite the important role of the interaction between the GB interface and point defects in mechanical properties relative few experimental studies about were published. With the advent of highly powerful computers, simulation at the atomic level can play an increasingly prominent role as an effective alternative to experimental observations. Contemporary computer modeling techniques based upon first principles of quantum mechanics (*ab initio* techniques) provide very accurate and consistent predictions for complex systems. *Ab initio* calculations have been used with great success to study the vacancy formation energy and the vacancy-induced relaxation in different metals, the vacancy diffusion energy barrier, etc [12,13]. On the other hand, the heavy computational demands of full-blown *ab initio* computation restrict its use to the study of relatively small systems and relatively few configurations. To make the progress in the simulation of large systems we could use a compromise between the computational rigorousness and efficiency. The techniques using the compromise contain fitting parameters in the interatomic potential. The potential is determined from experimental or *ab initio* database, which include physical quantities and may provide a good description of the energetic of a system. At present many of excellent potentials are derived for fcc metals using embedded atom method (EAM potential) [14]. The EAM potential combined with the Monte Carlo simulation predicts the GB energy in aluminum and copper in excellent agreement with the *ab initio* value [15]. The vast majority of simulations on GBs have been concerned with the equilibrium structure at zero temperature. Application of EAM method in combination with Monte Carlo technique enables to evaluate the effect of elevated temperature. Simulations on aluminum [16] and copper [17] showed good agreement with both experimental and *ab initio* results. The influence of elevated temperature enables to discover a new effect in the process of GB migration and interaction between the GB and point defect [18]. Before the concluding it should be noted that the techniques based on EAM potentials are less computationally demanding but also less rigorous that *ab initio* methods. The aim of this paper is to compare the mechanism of relative vacancy migration in copper reported recently [18] with the results of the *ab initio* simulation. The combination of both techniques could shed light on the physics behind the GB migration and mechanism of relative vacancy migration. The remainder of the article is organized as follows: The computational methodology, the details of GB construction and GBS simulation are discussed in Sec. II. In Sec. III, we discuss the equilibrium structure, sliding and energy of a vacancy containing interface. In Sec. IV, a summary and statement of conclusions are presented.

II. Computational technique

Our calculations were performed in the framework of a Σ5 tilt GB connecting the two copper surfaces of a plate. The boundary was obtained by rotating two perfect copper crystals with (0 0 1) face by an angle of 53.13^{o} with respect to each other about the interface. The lattice constant was set to the equilibrium value of 3.615 Å. 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.

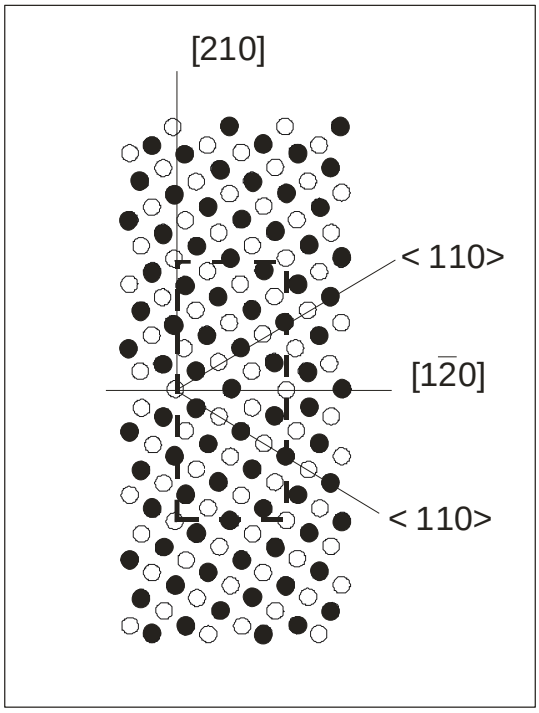

Fig.1 *Relaxed geometry of 160 atom supercell for the Σ5 tilt GB in copper viewed along the [100] direction. Atoms located in different planes perpendicular to the <110> direction are shown with filled and open circles. Dashed box denotes the supercell of 44 atoms used in LDA calculation.*

The atomic interaction in copper is described by a semiempirical many-body potential of the EAM. Potential used in this work was developed by Mishin *et al*. [19] on a large set of experimental and *ab initio* database. 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 Tab.1 we list the data computed using the EAM potential in comparison with the values predicted by *ab initio* method and experiment.

The geometry optimization has been made by simulating annealing (SA) technique introduced by Kirkpatrick, Gelatt, and Vecchi [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 350×10^3 steps. 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 J/m^2. The accuracy of the least-squares fit of the extrapolated zero-temperature GB energy is 7.32×10^{-3} J/m^2.

Tab. 1: *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.*

	This work	*ab initio*[(a)]	Experiment[(b)]
Lattice constant (Å)	3.615	3.61	3.62
Cohesive energy(eV)	-3.49	-3.54[(d)]	-3.49
Bulk modulus (GPa)	137	153-190	137
C' (GPa)	23.7	25.0-27.2	25.6[(c)]
c_{44} (GPa)	73.1	80.0-86.0	75.0[(c)]
$\Delta(E_{bcc}-E_{fcc})$ (meV)	42.7	6.8-48.8	-
$\Delta(E_{hcc}-E_{fcc})$ (meV)	444.8	506.0	-
Stacking fault energy (mJ/m^2)	39.5	-	45.0[(e)]
Vacancy: E_f (eV)	1.21	-	1.27[(f)]

[(a)]Reference [20], [(b)]Reference [21], [(c)]Reference [22]
[(d)]Reference [19], [(e)]Reference [23], [(f)]Reference [24]

For the modeling of vacancies in the grain boundary, a single vacancy is placed at two specified sites labeled by an integer *n*=0 and n=1, representing the *n*th layer from the grain boundary plane.

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 $[1\bar{2}0]$ direction. The sliding distance is described in percentage of a_{CLS}, where a_{CLS} is the lattice parameter of the Coincident Site Lattice (CSL) cell along $[1\bar{2}0]$ direction. The increment Δa=0.25Å (or 3.09 % of a_{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.

The electronic structure of the grain boundary is calculated by means of the pseudopotential plane wave method based on the density functional theory (DFT) and the local density approximation (LDA). We employed the exchange and correlation potential of Ceperly and Alder as parameterized by Perdew and Zunger [25] and the norm-conserving pseudopotential of Troullier-Martins [26]. The Kohn-Sham wave functions are expanded in plane waves with a kinetic energy cutoff of 100 Ry. For simulation we used 44 atoms taken from full relaxed supercell of 160 atoms. The supercell is bordered in Fig. 1 by dashed line. The atoms are distributed in 20 <210> layers parallel to the interface and were not relaxed during the *ab initio* calculation. The dimensions of the supercell along the $[\bar{1}20]$, [001] and [210] directions are 10.09 Å, 3.61 Å, and 20.18 Å, respectively. Because of the periodic boundary conditions, two calculations are needed to GB energy – one for the no relaxed GBs at the top and bottom side and another for the relaxed GB in the middle of the supercell. The GB energy (ΔE_{GB}) is computed

$$\Delta E_{GB} = (E_{GB}^{R} - E_{bulk}) - \frac{1}{2}(E_{GB}^{N} - E_{bulk})$$

where E_{GB}^{R} is the total energy of 44 atoms taken from relaxed 160 atom supercell at temperature of 27K, E_{GB}^{N} is the total energy of 44 atoms in no relaxed position and E_{bulk} is the total energy of 44 atoms in the bulk. The computed values of E_{GB}^{R}, E_{GB}^{N} and E_{bulk} are -2364.70036 Ha, -2364.69257 Ha and -2365.2787 Ha. It should be noted that the configuration was originally relaxed at elevated temperature of 27 K using EAM potential. Beside the energy LDA calculation also yields valence electron-density distribution.

III. Grain boundary equilibrium structure and interaction with the vacancy

In Fig. 2 we show the equilibrium GB electron densities in the form of contour plot (left panel) and the energy of each atom labeled with a different level of gray (right panel). The higher atomic energy corresponds with the higher electron density across the interface. On the other hand, low electron density (corresponds with the open area at the core) invokes very small change in atomic energy. The final equilibrium structure shows that the displacements away from the starting structure are small and most of the atomic movement occurs near the GB plane. The relative variation (strain) of the interlayer spacing as a function of the layer away from the GB plane 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. The fast decay of these functions indicates that the atomic relaxation and changes in the electron density are localized only within few layers from the interface. The atoms adjacent to these layers are probably responsible for the special properties of the material with GB.

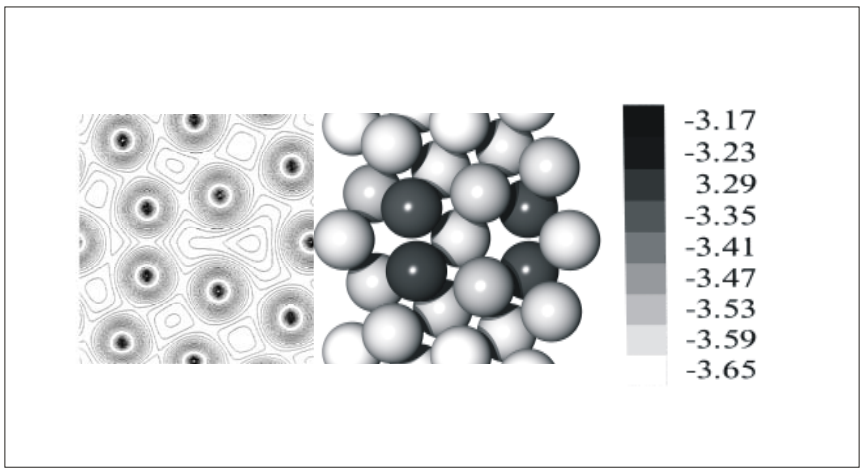

Fig. 2 *Electron density plot (left panel) and energy of each atom (right panel) for Σ5 tilt GB in copper viewed along the [100] direction. The atoms in right panel are labeled with a different level of gray, which represents the energy of each atom in the structure according to the energy scale (in eV) panel. The GB energy computed using LDA technique gives* ΔE_{GB}^{LDA} *= 1.195 J/m*^{2} *which is in good agreement with the value* ΔE_{GB}^{EAM} *= 1.09 J/m*^{2} *computed by EAM technique.*

It has been shown that GBS is associated with GB migrations and discontinuous changes of the GB energy at certain sliding distances. 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 situation is obviously more complicated if a vacancy is formed close to the GB. In general the lateral shift is associated with the GB migration as in the case of the vacancy free interface. In Fig 3 is shown 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. Surprisingly large change in energy is accompanied by defect migration from the sites that can not support a stable position to the site with a stable configuration. As we reported very recently [18] the vacancy, originally placed in the GB plane is transformed through a heavily perturbed configuration to the stable position in the first plane. 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 referred as relative vacancy migration.

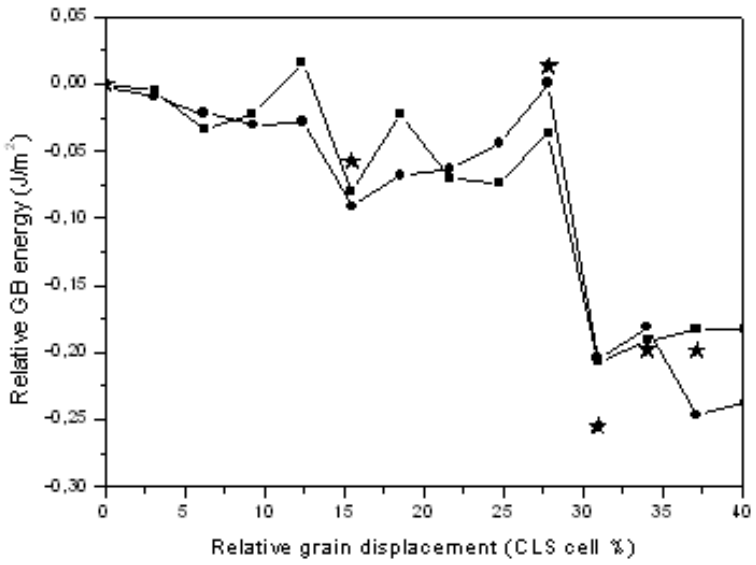

Fig.3 *Variation of the grain boundary energy in the presence of a vacancy as a function of the sliding distance expressed as a percentage of the lattice parameter a_{CLS} of the CLS along $[1\bar{2}0]$. The circles and squares denote result of EAM calculation using supercell of 159 atoms and 43 atoms, respectively. The stars denote result of LDA calculation using supercell of 43 atoms.*

The effect of relative vacancy migration was observed in numerical experiment based on EAM potential. As has been mentioned before, such type of potential contains empirical parameters. For this one should be prudent about the quantitative accuracy of such methods applied to complex GB-vacancy systems. To shed light in this question we employed more sophistic LDA technique. The supercell of 43 copper atoms was extracted from relaxed 159 atom cluster at certain sliding distances. In

particular, we used the configuration at 0%, 15%,27%,30%,34% and 37% of the lattice parameter, a_{CLS}. The atom positions were not more relaxed and GB energy for each configuration was computed by LDA technique. The result of relative ΔE_{GB}^{LDA} as a function of sliding distance is plotted in Fig. 3. Good agreement between the LDA and EAM results is well observed.

IV. Conclusion

We have studied the interaction between vacancies and the Σ5 tilt grain boundary in copper, using *ab initio* pseudopotential calculations, which yield reliable results for both the atomic structure and energetics compared to EAM semi-empirical atomistic approaches. The results indicates that EAM potential is able to describe both short range interactions which are responsible for the interface geometry and long range interactions responsible for GB energy. Main result of this work is that we confirmed the effect of relative vacancy migration. The result shows that certain sites closed to the GB are populated by vacancies during the deformation process by relative vacancy migration.

We believe that the simulation approach (combination of EAM and LDA technique) introduced in this work for vacancy and GB migration has a larger area of applications at low and mediate temperatures. At high temperatures, the results will be probably less accurate for the following reasons: (i) large number of different configurations must be generated to have good statistics, (ii) interactions between defects may start to play a role as the temperature increases, (iii) effect of anharmonicity may affect the GB – vacancy interaction.

Finally, we would like to note the phenomenological aspect of the study described in this paper. The model of relative vacancy migration proves to be capable of describing the experimentally observed phenomenon of heterogeneous population of GB by vacancies. This shows that the mechanical deformation process in combination with the GB migration plays a determining part in the formation of the radiation defect clusters along the interface. From point of view the ITER technology it means that mechanical load could change the radiation defects distribution and structural properties of the used materials.

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