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Impact of segregated interstitials on structures and energies of tilt grain boundaries in Mo

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ABSTRACT

In this work we investigate evolution of grain boundary properties as a result of interstitials' segregation. Both symmetrical and asymmetrical boundaries were considered. Interstitials were absorbed in a diffusive manner. The results of the conducted atomistic modeling reveal the ability of symmetric grain boundaries to recover their structure after segregation of a certain number of defects. Asymmetric boundary, which is scrutinized in this paper, does not clearly demonstrate reconstruction, but increase in its potential energy or any other evidences of growing instability were also not observed. For both symmetric and asymmetric boundaries several distinctive modes of interstitials' segregation can be determined.

1. Introduction

To the present day a lot of experiments on materials irradiation have been conducted. Available experimental data indicate that specimens with developed microstructure, in general, more resistant to radiation-induced swelling and embrittlement [1–5]. This promising property of microstructure elements is provoked by their ability to absorb point defects formed in displacement cascades during irradiation. Particularly, grain boundaries' (GB) can serve as internal sinks for vacancies, interstitials and their clusters [1].

Sink abilities of grain boundaries are confirmed experimentally by observation of denuded zones [6,3,7] – regions with reduced concentration of defects' clusters. Another experimental evidence is reduced density and size of the clusters in nanocrystalline material compared to coarse-grained specimens [1,8].

However, absorption of defects on grain boundaries can play a negative role. For instance, accumulation of He on GBs induces bubble formation [9–11] which promotes embrittlement, creep and intergranular fracture [2,12,13]. Thus, sink properties of GBs should be tuned properly to exploit positive, but elude negative effects.

Molecular dynamic study of GBs' sink properties [14,15] reveals good agreement between sink strength obtained from the rate theory and simulation results. It is also shown that at the steady state of irradiation, when vacancies and interstitials are segregated at the same rate, GBs' structures are not altered. However, at the temperatures considered in [14,15] GB is premelted and has amorphous structure, thus, no defects' clusters can be formed on it. Consequently this results cannot be extrapolated to the range of lower temperatures, where GB has more regular structure. Atomistic simulations at lower temperatures revealed some peculiarities of defects' absorption and recombination mechanisms. It is shown, that interstitial can make long non-diffusive hops to the boundary [16], or, on the contrary, pre-loaded interstitials can be emitted from the boundary to annihilate with bulk vacancies [17]. The ability and range of interstitial emission depends not only on the number of pre-loaded defects, but also on the grain boundary type and inclination angle [18,19], which is confirmed experimentally by variations of the width of denuded zones [7]. The general conclusion from the works [16–19] is that sink properties of GBs strongly depend on the boundary structure and can change significantly as a result of defect's absorption. These papers shed light on the effect of grain boundary structure on segregation, however, it remains unclear how segregation affects grain boundary structure.

In this work we investigate the impact of segregated interstitials on the structures of tilt grain boundaries in molybdenum. The subject is indeed intriguing because variation of local atomic density on GBs, driven by defect segregation, can lead to structural

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phase transitions [20]. Interstitials are considered because of unbiased absorption over vacancies during relaxation of collision cascades [19,21] and because of the pre-loading effect [17].

2. Methodology

The molecular dynamics (MD) simulations were performed using the LAMMPS code [22]. We employed interatomic potential for molybdenum [23], which was optimized for describing elastic properties, point defects' formation energies and liquid state.

The simulation block used in this work is shown on Fig. 1. It consisted of two grains, which were rotated around [001] and joined together, to make a tilt GB. Hence the usual geometric construction method was employed, it is described in detail elsewhere [24]. Particularly, it is shown that the construction method and chosen interatomic potential reproduce experimentally observed grain boundary structures.

Periodical boundary conditions along all three dimensions were applied, consequently, we have two grain boundaries in the simulation domain (denoted as GB on Fig. 1). This was done to introduce additional degree of freedom in the system: we do not have fixed atoms in the domain, so the grains can slide or rotate, if needed. Dimensions of the computational cell vary depending on simulation, the minimum values used were $(L_x \times L_y \times L_z)_{min} = 2.1 \times 9.4 \times 2.5$ nm, which indeed exceed the potential's cut-off distance of 0.56 nm.

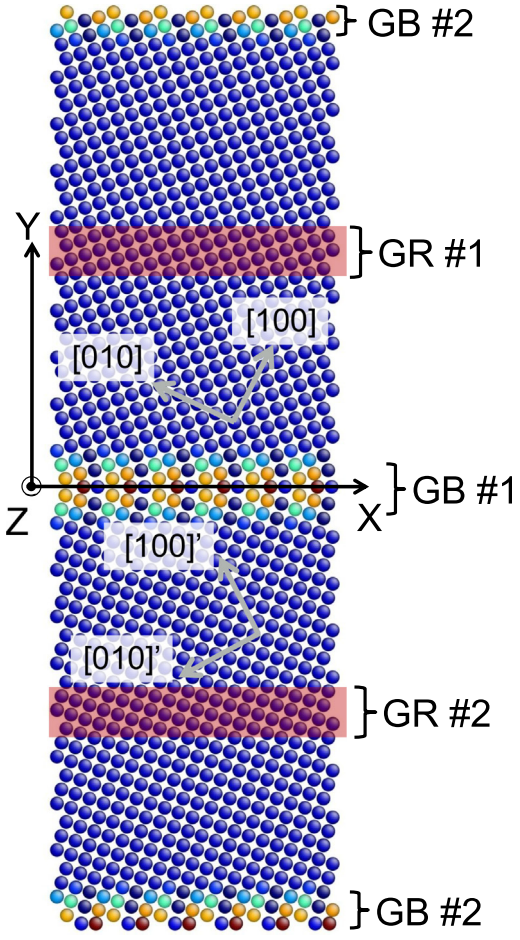

Fig. 1. Scheme of the computational cell. Atom color corresponds to its potential energy. GB denotes grain boundary position, due to periodic conditions there are two of them in the cell. Tilt axis of the boundary is parallel to *Z*. In both of the grains [100] and [010] directions are indicated by gray arrows. Defects were generated inside two regions denoted as GR #1 and GR #2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In order to investigate the impact of segregated interstitials on structure and properties of grain boundary, series of simulations were performed. Each of the simulation consists of several steps:

1. Generate initial structure.
2. Inject two interstitials, one inside each of the grains.
3. Perform MD run. Store snapshot of the system after the run.
4. Repeat 2–3 until required.
5. Minimize the stored snapshots.

On the first step, we obtain all the necessary information about equilibrium grain boundary structure and its energy. Further, we will refer to this data during potential energy calculations and structure analysis.

On the following step of the simulation interstitials are introduced. This is made by addition of extra atoms at random positions inside both generation regions (denoted as *GR* on Fig. 1). The generation regions are located equidistantly from both of the grain boundaries. Distance between GR and grain boundary is chosen big enough, so that introduced interstitial initially does not interact with GB, interaction becomes significant only when the defect diffuses close enough to one of the boundaries. The distance estimation is based on the simulation box spatial potential energy profiles. To avoid atom overlapping, potential energy of the system is minimized (here and further via Polak–Ribiere conjugate gradient algorithm). After energy minimization, the simulation cell is equilibrated to desired temperature and, in some of the simulations, pressure.

To trace further evolution of the system the Parallel Replica Dynamics (or PRD) method [25] is used, which allows to speed up molecular-dynamic calculations significantly. The system evolution trajectory is calculated in microcanonical ensemble at 1000 K for approximately 120 ps, which is enough for interstitials to diffuse from generation region to grain boundary (if the latter still acts as a sink). Such generation rate corresponds to accumulation dose rate about 10^5 dpa/s which is about 14 orders of magnitude higher than typical value for light water reactor [26].

After PRD simulation is finished, we create a snapshot of atoms' positions and velocities. At the next step of the simulation another pair of interstitials is introduced, system is equilibrated again, another PRD run is conducted and another snapshot is generated. This loop is repeated for 100 iterations or more. Note, that the obtained snapshots of the system correspond to consequential states of the bicrystal with increasing number of introduced interstitials.

The final stage of our simulation is the snapshots' potential energy minimization. This minimum-energy configurations were analyzed in detail, the results of this analysis are discussed in the next section.

3. Results and discussion

In the current paper two symmetric and one asymmetric tilt grain boundaries were investigated (α – misorientation angle): $\Sigma5(310)$ $\alpha = 36.8^\circ$, $\Sigma5(210)$ $\alpha = 53.1^\circ$ and (100) $\alpha = 36.8^\circ$. Analysis of the minimum-energy configurations corresponding to different number of defects segregated at the GB revealed consistent results for both symmetric boundaries. Therefore in case of symmetric grain boundaries only $\Sigma5(210)$ will be discussed.

3.1. Symmetric boundaries

Initial $\Sigma5(210)$ structure is shown on Fig. 2a. When concentration of interstitials on the GB increases, defects start to form