New physics of grain boundaries in bcc metals from the atomic-level: molybdenum as a case study

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We present a systematic trend study of the symmetric tilt grain boundaries about the ⟨110⟩ axis in molybdenum. Our results show that multiple structural phases, some incorporating vacancies, compete for the boundary ground state. We find that at low external stress vacancies prefer to bind to the boundaries in high concentrations, and moreover, that external stress drives structural phase transitions which correspond to switching the boundaries on and off as pipe-diffusion pathways for vacancies. Finally, we present physical arguments which indicate these phenomena are likely to occur in the other bcc transition metals as well.

I. INTRODUCTION

Molybdenum, with its high melting point and relatively inert chemical nature is often considered for high-temperature structural applications, but its extreme brittleness limits its usefulness. Experimental studies [14] demonstrate that this brittleness is an intrinsic property of the material and largely unrelated to the presence of impurities. These studies suggest, moreover, that this brittleness arises from weak inter-granular cohesion along the grain boundaries [15]. In this work, we shed light on the microscopic physics of these boundaries by presenting a detailed, atomic-level trend study of the behavior and structure of their low energy phases and the transitions among these phases.

This study reveals new physics in the interaction of the grain boundaries with vacancies. The traditional mechanisms of interplay between vacancies and grain boundaries include pipe diffusion of vacancies along the boundary [14, 15], and absorption and emission of vacancies during continuous climb of primary or secondary dislocations [16]. We find, in addition, that boundary vacancies prefer to collect together at high densities on the boundary plane. Our results also indicate that grain boundaries can either emit or absorb large concentrations of vacancies into the surrounding bulk while undergoing structural phase transitions under applied stress. While our focus in the present study is on the particular system of symmetric tilt boundaries around the ⟨110⟩ axis in molybdenum, which are known to dominate the recrystallization texture of this material [15], we expect for reasons detailed below that these conclusions hold quite generally for symmetric tilt boundaries in bcc materials.

II. PROCEDURE

The heavy computational demands of full-blown ab initio electronic structure calculations [17] and semi-empirical tight-binding models [18, 19] restrict their use to the study of relatively small systems and relatively few configurations. In order to understand complex processes such as fracture, dislocation migration and inter-granular cohesion, computationally more feasible empirical potentials must be used. Moriarty has developed such an empirical model based on a multi-ion interatomic potential developed from first principles generalized pseudopotential theory [17]. The resulting model generalized pseudopotential theory (MGPT) potential successfully predicts the cohesive, structural, elastic, vibrational, thermal and melting properties of molybdenum [19] as well as the ideal shear strength and self-interstitial and vacancy formation energies [20]. We use this potential throughout this work.

Focusing on the ⟨110⟩ symmetric tilt boundaries, we consider Σ=3(112) and Σ=9(114), which are among the lowest in energy, and Σ=3(111), Σ=9(221), Σ=11(113) and Σ=11(332) as examples of boundaries with higher energies. To study the physics of these boundaries, which reside in bulk material, we employ periodic boundary conditions as the most natural. To minimize boundary-image interactions, we always maintain at least seventeen layers of atoms between boundaries in our supercells. Determination of the ground state and the low energy excited state structures in principle requires the exploration of the phase space of all possible configurations, which is an impractical task without taking into account some basic physics. The primary consideration we use to restrict this phase space is that, due to the relatively strong directional bonding in molybdenum and similar bcc metals, the structure of the grain boundaries tends to preserve the internal topology of individual grains. Under this restriction, there remain then only three considerations for each boundary: (1) possible addition and removal of atoms to and from the faces of the grains at the boundary, (2) the displacement of the grains relative to one another, and (3) relaxation of the internal atomic coordinates.

For the first consideration, the fact that the interstitial energy in molybdenum (≥10eV) is much larger than the vacancy energy (3eV) [20] indicates that insertion of additional material at the boundary leads to unlikely
high interfacial energies. We therefore concentrate only on the removal of atoms at the boundary. Direct calculations with the MGPT potential reveal that the most favorable sites for atom removal are in the vicinity of the boundary. It turns out that, because the atoms in the planes adjacent to the boundary plane (indicated by circles in Figure 1a) pack closely together, these sites are the energetically most favorable for vacancy formation.

This leads us to consider the following structural phases for the boundaries in our study: grains joined with the amount of material expected from the naive coincident site lattice (CSL) construction ("full-material phase"), and boundaries where we remove atoms from the circled sites in Figure 1a, which shows this construction. Below, we find that binding energy per boundary vacancy is higher when vacancies collect together at high density on the boundaries. Therefore, we first concentrate on boundaries with high vacancy densities. Because removal of an entire plane of atoms near the boundary is topologically equivalent to the initial "full material" phase under appropriate relative displacement of the grains, we focus on the phase where we remove one half-plane of atoms from the layer adjacent to the boundary ("vacancy phase").

To determine the ground state of the above two structural phases, we next turn to the second consideration above, the relative shifts of the grains. The displacement-shift complete (DSC) cell, which we explore on a 16 × 16 sampling grid (which reduces to 4 × 4 by symmetry), contains all possible unique relative plane shifts of the grains. For each such shift, we complete our search and address the third and final consideration by performing full relaxations of both the perpendicular expansion of the grains and their internal coordinates. This extensive survey requires force and energy calculations of approximately 100,000 boundary configurations, and would be infeasible to carry out with electronic structure techniques.

To confirm the effectiveness of this survey in identifying ground state structures, we repeat the above procedure with supercells in which we remove an entire plane of atoms from the boundary. For all six boundaries in our study, our procedure indeed identifies the appropriate shift to recover the initial, topologically equivalent ground state found for the full-material phase before the removal of the plane of atoms.

III. RESULTS

A. Low Energy Phases

Our results reveal several general trends in the physics of the ⟨110⟩ tilt grain boundaries in molybdenum. As a specific example, consider the Σ=9(114) boundary, which Figure 1 shows. Panel (a) shows the naive CSL construction of the full-material phase, whose ground state as identified through our procedure, appears in Figure 1b. We find that this phase lowers its energy through both a perpendicular expansion of the boundary and integral shifts parallel to the boundary, both of which tend to increase the local volume for the closely packed atoms near the boundary plane, restoring them to a more bulk-like environment.

Table I shows that the outward expansion is a general trend among all grain boundaries in our study and that shifts occur along the boundary in the direction perpendicular to the tilt axis (y-direction, Figure 1) to allow for a more bulk-like local environment. We find no significant shifts along the tilt axis (z-direction, Figure 1) for this phase of any of the boundaries. Finally, the last column of the table gives the mechanical compliance ((1/k)) of each boundary, where k is determined from the quadratic response of the energy per unit area per boundary as the cell expands, which takes the form

\[ \Delta U = \Delta U_0 + \frac{1}{2}k(x - \Delta x)^2 + \ldots \]  

(1)

where x is the expansion of the cell, and Δx and ΔU0 are the relaxed perpendicular expansion and boundary energy given in the table, respectively. The table lists the difference between 1/k for the boundary and for the

FIG. 1. Structural phases of the Σ=9(114) grain boundary: (a) naive CSL boundary, (b) relaxed full-material boundary, (c) relaxed vacancy phase boundary. (To aid visualization, atoms from the two cubic sublattices are colored separately, light and dark.)

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Turning now to the vacancy phase, Figure 1b shows the results of our ground-state search for the $\Sigma 9(114)$ boundary as formed by removing the circled atoms from Figure 1a. We now find grain-shifting as well as local internal relaxations to create more bulk-like local atomic environments, and as Table II summarizes, we again find this behavior for all boundaries in our study. The perpendicular shift is always inward compared to the ground state of the full-material phase, so as to close the material void associated with the vacancies. Finally, we frequently find for the vacancy phase, even for the highly stable $\Sigma 3$’s, parallel shifts relative to the full-material phase which produce more natural bonding arrangements for the boundary to accommodate the vacancies. This tendency for accommodation is so strong as to induce the only shift along the tilt axis we observe in this study, for the vacancy phase of the $\Sigma 11(332)$ boundary.

Figure 2 compares the ground-state boundary energies of the various phases. In all cases, we find the full-material phase (black bars) to be lower in energy than the vacancy phase (hatched bars), although often not by far. As in the experimental case, the lowest ground state interfacial energy occurs for the naturally occurring twin $\Sigma 3(112)$ boundary [3]. Moreover, apart from this twin, all remaining ground state boundary energies are fairly constant (within 25%), as also found in experiment (within 30% [3]).

Figure 3 presents another relevant comparison. To verify, as mentioned above in Section II, that boundary vacancies indeed prefer to cluster together, we have also considered boundaries with nearly isolated vacancies within our supercell approach. Table V presents energy, displacement and compliance results for boundaries where the vacancy concentration (3.3%) is one fifteenth that of the boundary-vacancy phase. Table V presents the analysis of this data. As the larger binding energies reflect, the concentrated phase is more stable. This added stability appears to arise from the structural relaxation through parallel shifting of the grains observed in Table III, made possible by the high density of vacancies. Finally, we note that in the extreme case of the $\Sigma 11$ boundaries, vacancies do not even bind to the boundary at low densities.

### B. Phase Transitions

Three trends which the preceding results exhibit can be expected from general, material-independent considerations: (1) that the boundaries present preferred binding sites for vacancies because they disrupt the bulk bond-order, (2) that boundary vacancies prefer to collect into the high-density vacancy phases because of the additional relaxation, which parallel shifting of the grains affords, and (3) that the binding of vacancies to the boundary reduces the intergranular spacing because this restores more bulk-like interatomic separations. These phenomena open the intriguing possibility that the application of tensile stress normal to grain boundaries in bcc metals generally drives transitions among these various structural phases, thereby providing new forms of boundary-vacancy interaction.

To explore this possibility, we consider the thermodynamic potential which is minimized under fixed external stress, the enthalpy. As a function of applied perpendicular stress $\sigma$, the enthalpy of a grain boundary structure relative to bulk is

$$\Delta H = \Delta U_o - \sigma \Delta x - \frac{\sigma^2}{2} \Delta (1/k) + O(\sigma^3). \quad (2)$$

Here $\Delta U_o$ is the difference in the ground-state energy per unit area, $\Delta x$ is the difference in preferred perpendicular intergranular separation, and $\Delta (1/k)$ is the difference in compliance. Each of these materials parameters appears for each relevant phase in Tables II-V.
As an example, Figure 3 shows the behavior of the enthalpy, relative to bulk, of the naturally occurring Σ3(112) boundary in its full-material, vacancy and bulk-vacancy phases. Three first-order phase transitions (enthalpy crossings) are evident in the figure. At zero stress, as observed above, the full-material phase is the ground state of the boundary, and moreover, in the presence of vacancies, the vacancy phase has lower energy than the bulk-vacancy phase, indicating that vacancies prefer the boundary over the bulk. However, at an applied stress of about 18 GPa, the Σ3(112) boundary system undergoes a first-order phase transition in which the vacancy phase is no longer preferred, and the boundary ejects its vacancies into the surrounding bulk material. A second transition occurs near 25 GPa, at which point the bulk-vacancy phase becomes lower in enthalpy than the bulk material phase. This corresponds to the spontaneous formation of vacancies in bulk, indicating breakdown of the bulk material. The third transition occurs near 30 GPa. Were this transition accessible before the breakdown of the bulk material, it would correspond to spontaneous formation of boundary vacancies.

Table IV presents the stresses for the above three transitions for all boundaries in our study. In all cases, the emission stress is accessible before breakdown of the bulk material through spontaneous formation of vacancies. Moreover, except for the outlying behavior of the Σ9(221) boundary, vacancies always first form spontaneously in the bulk before they do so on the boundaries.

To verify that these results are not artifacts of the high-density vacancy phase, we repeat the above enthalpy analysis for boundaries with low densities of vacancies using the data of Table VI. As Table VII summarizes, we again observe the same transitions. The Σ11 boundaries do not bind vacancies at low concentrations (Table V), and therefore, the transition stresses for the emission of vacancies for these boundaries are not physically relevant. For the lower Σ boundaries (except the Σ9(221) boundary, which again exhibits an outlying behavior), diluting the vacancy concentration reduces the critical emission stress at which the boundaries emit boundary vacancies into the bulk (σ\text{emit}), thus making this transition more accessible.

Finally, as we expect from the fact that boundary vacancies are more stable in high concentrations, the stress required to induce formation of vacancies on the boundaries (σ\text{tear}) at low densities is generally greater than for the high-density vacancy phase. As a last consistency check on our analysis, we note that the breakdown stress for the bulk (σ\text{break}), as a characteristic of the perfect crystal and not the boundary, remains essentially unchanged between the two independent sets of calculations for low and high boundary vacancy concentrations.

IV. CONCLUSIONS

Several general conclusions reached in the discussion above are supported both by trends in our calculations for a specific set of boundaries in molybdenum and by quite general, material independent arguments. We expect that the following conclusions likely hold generally for the interactions among vacancies and tilt grain boundaries in bcc transition metals: (1) consistent with the traditional view of grain boundaries as diffusion pathways, vacancies prefer the boundaries over the bulk at low stresses, (2) boundary vacancies prefer to collect into high-density vacancy phases, (3) application of sufficient tensile stress to a boundary induces a structural phase transition which drives the vacancies from the boundaries into the bulk, thereby shutting off pipe diffusion along the boundary. The last of these conclusions in particular may have important implications for crack growth through pipe-diffusion assisted void growth and void formation at grain boundaries.

Finally, in terms of precise quantitative predictions of the critical stresses characterizing these phenomena, it is important to bear in mind that the particular interatomic potential which we have employed (MGPT), although one of the most reliable, is known to exaggerate energy scales for complex structures [21]. We therefore would expect to find these same transitions, but most likely at lower stresses, when studied either experimentally or \textit{ab initio}.

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| Boundary | $\Delta u_o$ [mJ/m$^2$] | $\Delta x$ [Å] | $\Delta y$ [Å] | $\Delta z$ [Å] | $\Delta (1/k)$ [mJ/m$^2$/Pa$^2$] |
|---------|-----------------|---------|--------|--------|------------------|
| $\Sigma 3(112)$ | 610 | 0.1 | 0.3 | 0.0 | 900 |
| $\Sigma 3(111)$ | 2020 | 0.5 | 0.0 | 0.0 | 4770 |
| $\Sigma 9(114)$ | 1730 | 0.5 | 0.1 | 0.0 | 3410 |
| $\Sigma 9(221)$ | 2180 | 0.4 | 0.1 | 0.0 | 100 |
| $\Sigma 11(113)$ | 1740 | 0.5 | 0.2 | 0.0 | 1460 |
| $\Sigma 11(332)$ | 2160 | 0.4 | 0.5 | 0.0 | 580 |

*TABLE I. Full-material phase: energies ($\Delta u_o$), perpendicular expansions ($\Delta x$), and shifts ($\Delta y$ and $\Delta z$) relative to the CSL construction, and compliances relative to bulk ($\Delta (1/k)$), where coordinates are as defined in Figure 4.

| Boundary | $\Delta u_o$ [mJ/m$^2$] | $\Delta x$ [Å] | $\Delta y$ [Å] | $\Delta z$ [Å] | $\Delta (1/k)$ [mJ/m$^2$/Pa$^2$] |
|---------|-----------------|---------|--------|--------|------------------|
| $\Sigma 3(112)$ | 720 | 0.1 | 0.3 | 0.0 | 950 |
| $\Sigma 3(111)$ | 2076 | 0.5 | 0.0 | 0.0 | 2600 |
| $\Sigma 9(114)$ | 2360 | 0.4 | 0.1 | 0.0 | 3520 |
| $\Sigma 9(221)$ | 2200 | 0.3 | 0.1 | 0.0 | 260 |
| $\Sigma 11(113)$ | 1900 | 0.5 | 0.2 | 0.0 | 1900 |
| $\Sigma 11(332)$ | 2250 | 0.4 | 0.5 | 0.0 | 990 |

*TABLE IV. Bulk-vacancy phase: energies ($\Delta u_o$), perpendicular expansions ($\Delta x$), and shifts ($\Delta y$ and $\Delta z$) relative to the CSL construction, and compliances relative to bulk ($\Delta (1/k)$), where coordinates are as defined in Figure 4.
| Boundary | Binding energy per vacancy at high density [eV] | Binding energy per vacancy at low density [eV] |
|----------|-----------------------------------------------|-----------------------------------------------|
| Σ3(112) | 0.7                                          | 0.6                                           |
| Σ3(111) | 2.1                                          | 1.1                                           |
| Σ9(114) | 1.4                                          | 0.7                                           |
| Σ9(221) | 2.3                                          | 2.0                                           |
| Σ11(113) | 1.4                                      | -7.1                                          |
| Σ11(332) | 1.4                                         | -1.7                                          |

**TABLE V.** Boundary-vacancy binding energies at high and low densities. (The Σ11 boundaries do not bind vacancies at low concentrations.)

| Boundary | $\sigma_{\text{emit}}^e$ [GPa] | $\sigma_{\text{break}}^e$ [GPa] | $\sigma_{\text{tear}}^e$ [GPa] |
|----------|-------------------------------|-------------------------------|-------------------------------|
| Σ3(112) | 18                            | 25                            | 30                            |
| Σ3(111) | 17                            | 24                            | not observed                 |
| Σ9(114) | 21                            | 23                            | 25                            |
| Σ9(221) | 38                            | 24                            | 10                            |
| Σ11(113) | 21                        | 28                            | 42                            |
| Σ11(332) | 31                        | 33                            | 35                            |

**TABLE VI.** Critical stresses for the phase transitions discussed in the text: emission of vacancies from the boundary into the bulk ($\sigma_{\text{emit}}^e$), breakdown of the bulk through spontaneous formation of vacancies ($\sigma_{\text{break}}^e$), formation of vacancies, and thus tearing, at the boundary ($\sigma_{\text{tear}}^e$).

| Boundary | $\sigma_{\text{emit}}^e$ [GPa] | $\sigma_{\text{break}}^e$ [GPa] | $\sigma_{\text{tear}}^e$ [GPa] |
|----------|-------------------------------|-------------------------------|-------------------------------|
| Σ3(112) | 16                            | 25                            | 32                            |
| Σ3(111) | 12                            | 24                            | not observed                 |
| Σ9(114) | 9                             | 23                            | 58                            |
| Σ9(221) | 44                            | 24                            | 8                             |
| Σ11(113) | 90                        | 28                            | 60                            |
| Σ11(332) | 125                        | 33                            | 52                            |

**TABLE VII.** Critical stresses for the same transitions as in Table VI, but at 3.3% vacancy concentration.