4.3 Ab Initio Study of Grain Boundary Properties of Tungsten Alloys —

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OBJECTIVE

The objective of this research is to support the search for tungsten alloys with increased grain boundary cohesion using ab initio methods.

SUMMARY

Density functional theory was employed to investigate the grain boundary (GB) property of W-TM alloys (TM: fifth and sixth row transition metals). GB strengthening was found for Hf, Ta, Nb, Ru, Re, Os and Ir for Σ27{525} and to a lesser degree for Σ11{323}. Lower valence solutes strengthen the GB at certain substitutional sites, while higher valence elements enforce it at other positions. For Σ3{112}, the alloys exhibit reduced cleavage energies. Hence, allowing with TMs increases the GB cohesion more effectively for large-angle GBs whose cleavage energy is, in general, inherently lower than the low-angle ones. Electron density analysis elucidates the mechanism of charge addition or depletion of the GB bonding region upon TM substitution at various positions leading to stronger or weaker intergranular cohesion, respectively.

PROGRESS AND STATUS

Introduction

The development of novel W-based materials that are suitable for future fusion reactors is likely to involve synergistic advancements in intrinsic W alloys [1, 2], grain boundary engineering [3, 4] and W-based composites [5, 6]. In all of these areas, understanding and controlling the characteristics of materials at intergrain regions are important. Alloying with Re has been shown to reduce the ductile-brittle transition temperature (DBTT) to 600°C and to increase the recrystallization temperature to 1400°C [1]. Recent ab initio study showed that Re significantly enhances the intergranular strength [7]. This study was intended to add to the body of knowledge of the effects of transition metals (TMs) on the grain boundary (GB) cohesion. We included three model structures namely Σ27<110>{525}, Σ11<110>{323} and Σ3<110>{112} and investigated the transition metals from the fifth and sixth row of the periodic table.

Formalism

Starting from general-twin slab configurations, molecular dynamics (MD) simulations were performed to search for the ground state structure of the GBs. We used the interatomic potential developed by Ackland and Thetford [8]. Systematic interfacial shifts and atoms relaxations were done to achieve the most stable configurations. The structures obtained from the MD were further optimized via ab initio method. VASP software was used to perform the quantum mechanical calculations based on the density functional theory (DFT). Accurate projector-augmented-wave pseudopotentials with Perdew-Burke-Ernzerhof exchange-correlation functionals were employed [9–11]. Plane-wave energy cutoffs and k-point sampling of the Brillouin zone were carefully checked for convergence. Structures were fully relaxed with a tolerance of 1 meV. For non-slab configurations, a force tolerance of 10 meV/A was used. At the end of volume-nonconserving relaxations, an additional static calculation was performed to avoid numerical errors due to basis incompleteness.

The necessary slab thickness for the DFT calculations was determined from the convergence tests of the {525}, {323} and {112} surface energies. A total of 62, 38 and 23 layers which include one GB interface and two free surfaces were required for the Σ27, Σ11 and Σ3, respectively. Supercells containing 124 (Σ27), 76 (Σ11) and 138 (Σ3) atoms were used to obtain planar concentrations of 1.37, 2.15 and 1.37 solute/nm^2, respectively. Using the atomic volume of bcc (0.016 nm^3), these concentrations correspond to a three-dimensional value of 2.6, 5.0 and 2.6 at. %.

RESULTS

Figure 1 shows the structure of the GBs as viewed from the <110> direction. The structures consist of two alternating layers along this direction which are represented by different colors. To study the cohesion, cleavage energies were calculated from the GB energy and the energies of the cleavaged halves. The cleavage plane was taken at a position indicated by the dashed line in Figure 1. Several GB sites were investigated as the substitutional positions. Representative transition metals from the fifth and sixth rows of the periodic table were studied. The results are presented on the right panel of Figure 1 and arranged with an increasing atomic number.

The results for the Σ27 have been presented in Ref. [7]. Five GB sites were studied for this GB. Three sites with distinct properties are included in this report to allow comparison with other GBs. In general, for each substitutional site, the cleavage energy forms a smooth curve as a function of the solute. The maximum of each curve represents the best GB strengthener for the corresponding site. Interestingly, a similar set of curves was observed for the fifth- and sixth-row solutes. This indicates that the effect of the TMs on the GB cohesion is closely related to the electronic valence and how the occupancy of the d-orbitals varies across different atomic environments. For all the three GBs, the sixth-row TMs exhibit higher cleavage energies than the corresponding fifth-row elements.

For Σ27 and Σ11, Ru, Re, Os and Ir considerably increase the cleavage energy when they are at position A, while Hf and Ta do so at position D. Zr and Nb also show a strengthening property at site A for Σ27. As we go from Σ27→Σ11→Σ3, the alloys become less effective. In fact, the data on Σ3 shows that very limited increase of cohesion was obtained with Ru, Re and Os at position F. Comparison of GB energy among different substitutional sites revealed that the more stable the site, the higher the cleavage energy. Therefore, energetically, the strengthening property of a solute is preferred even though there are spurious sites. This relation holds true for each solute. For Σ27, we have calculated segregation energies defined as the GB energies minus the energies of the solute if it were in the grain's interior [7]. These energies represent the stability of the substitution with respect to a bulk position. In general, higher valence TMs show more tendency to be at the GB.

Comparison with different concentrations showed that, at low concentration regime, the strengthening property is proportional to the planar concentration of the solute. In this regime, we have investigated the property of ternary alloys by placing Re, Or, or Ru at site A and Hf, Ta, or Nb at site D of the Σ27. The results showed a strengthening property of roughly the sum of contributions from each solute. This suggests that by employing both lower valence and higher valence solute, further improvements could be achieved. A significant increase of cleavage energy is indicated in several TMs for the Σ27. Meanwhile, for Σ3, the data show that most likely TMs have adverse effects on the GB cohesion. However, the cleavage energy of pure Σ3

is significantly higher than that of Σ27. In fact, even the worse case of decohesion in Σ3 (Pd) still exhibits a higher cleavage energy than the best case of cohesion in Σ27 (Os not Hf since Hf solubility is less than the simulated concentration).

The strengthening property of TMs in this study can be understood from the electron distribution plot. Figure 2 shows examples of such plot for Σ27 with Os or Hf at position A (left panel) or D (right panel). The charge density of the pure material is depicted in the center panel. GB bonds are indicated with the arrows. For position A, substitution of W with a lower valence element such as Hf results in a weaker bond since there are fewer electrons available for bonding. On the other hand, higher valence solutes such as Re and Os will strengthen the GB bonds. However, this trend does not continue towards Pt since most of the d-electrons are already paired and unavailable for bonding. For site D, the situation is reversed. Atom at this site is not responsible for GB bonds as much as atom at position A. Introduction of Hf at position D increases the charge density of the GB bonds. This indicates that electrons are partially transferred from Hf at site D to atoms at site A resulting in stronger bonds. Meanwhile, Os at position D tends to deplete the electrons from the bonding site A, lowering the GB cohesion.

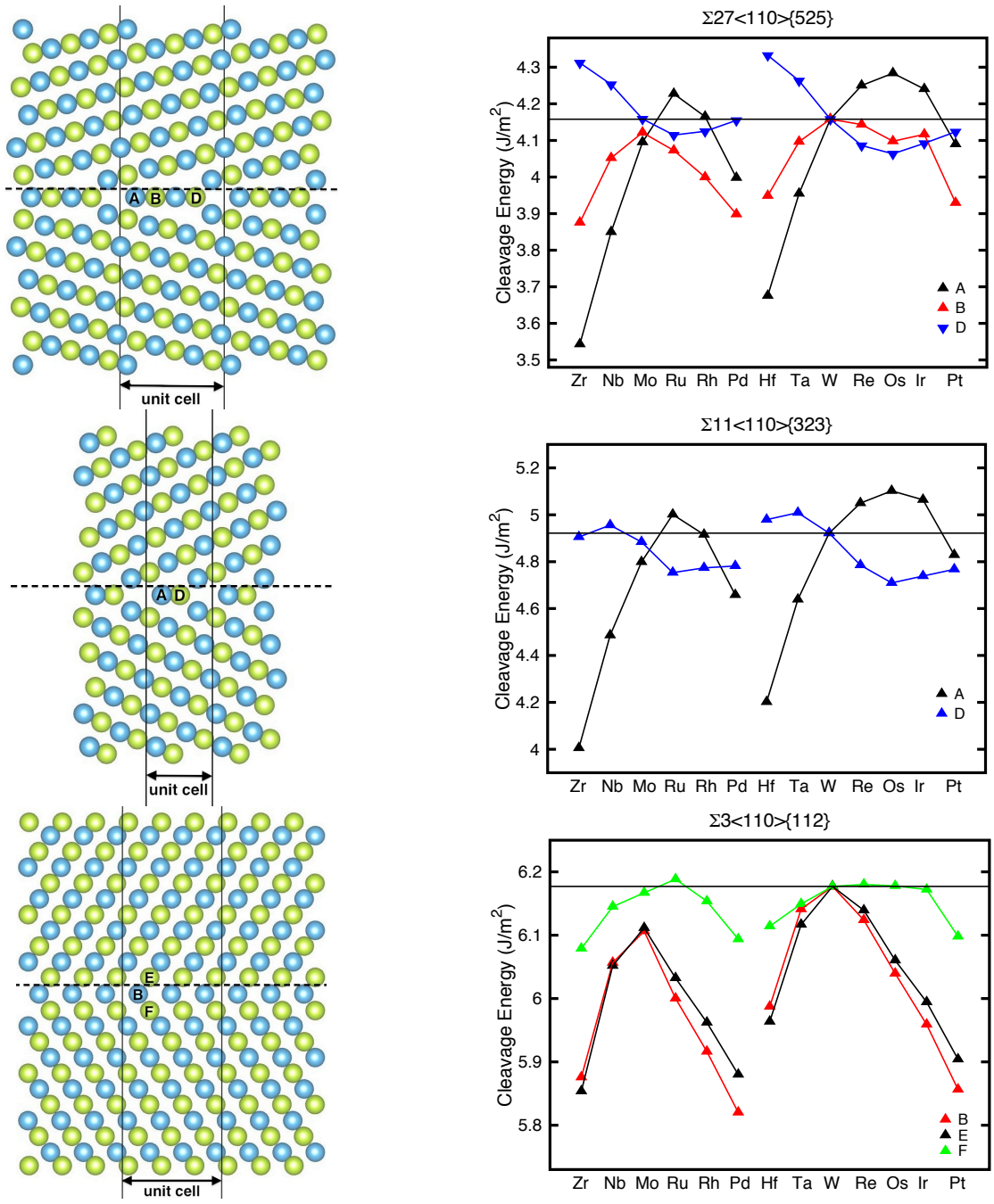

Figure 1. Grain boundary structures of W-TM alloys viewed from the <110> direction (left panel) and cleavage energies (right panel). The dashed line indicates the cleavage plane. The corresponding solute concentrations are 2.6 (Σ27), 5.0 (Σ11) and 2.6 (Σ3) at. %.

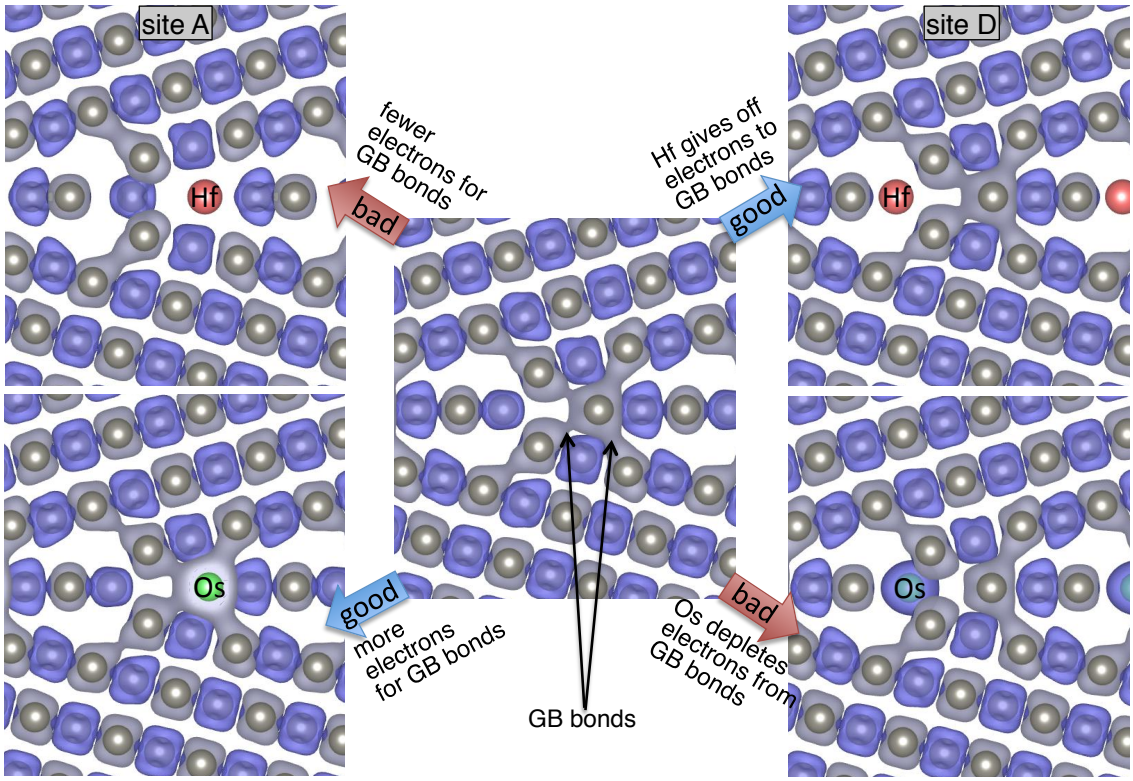

Figure 2. Electron density of the Σ27{525} grain boundary with Hf or Os at substitutional site A or D. GB strengthening is revealed by the charge increase in the GB bond regions.

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