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First-principles determination of grain boundary strengthening in tungsten: Dependence on grain boundary structure and metallic radius of solute

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ABSTRACT

The control of segregation-induced grain boundary (GB) strengthening is a strategy for improving the ductility and intergranular fracture of metals. In this work, by first-principles calculations we study the strengthening effect of transition metals on a series of tungsten GBs to uncover its dependence on the GB structures and the radius of solute itself. The results show that the GB strengthening depends strongly on the GB structures. The solutes tend to enhance cohesion for GBs with larger GB energies, while they decrease cohesion for those with smaller GB energies. In addition, it is generally found that for all GBs the strengthening energies of elements correlate positively with their metallic radii, implying that the size effect plays a major role in the GB strengthening in tungsten. By analyzing the strengthening effect of solutes at different segregated sites, we find that the oversized solutes (Zr, Nb, Hf, Ta) act as cohesion enhancers when segregated in the GB plane, while the undersized elements (Ru, Rh, Re, Os, Ir) strengthen the GBs at the nearest neighbor positions. Experimentally, we show that the presence of Zr/Ta/Re impurity, which leads to an increase of intergranular fracture, increases the theoretical tensile strength and the GB cohesion. These results suggest that the improved fracture resistance by Re, Ta and Zr originates mainly from the GB strengthening due to their segregation.

1. Introduction

Grain boundaries (GBs) are ubiquitous defects in metallic alloys and macroscopic strength of materials depends strongly on GB cohesion [1,2]. Small amounts of solute atoms can significantly change the fracture toughness and corrosion resistance of metallic alloys by several orders of magnitude (e.g., hydrogen embrittlement [1] and stress corrosion cracking [2]). These observations are commonly attributed to segregation of solutes at GBs and other interfaces [3,4].

Among the refractory transition metals, tungsten (W) is the most promising material for extreme environmental conditions occurring within fusion energy. W is being considered as the primary candidate material for plasma-facing components in future fusion reactors because of its excellent physical and chemical properties such as high melting point, low sputtering, and high neutron absorption [5,6]. However, W also exhibits serious irradiation induced brittleness which occurs mostly by intergranular fracture associated with weak GBs. Therefore, understanding and controlling the properties of W materials at GB regions is highly valued, especially for the effect of impurities on the GB strength.

Since it is difficult to obtain effective information on the effects of impurity atoms on GB strength experimentally, theory study via first-principles calculations provides useful insight into the mechanism controlling the strength, toughness, and resistance to impurity embrittlement. Simulation studies have successfully used to study effects of solutes on GB strength in many metals such as Fe [7–9], Al [10–12], Ni [13–16], Cu [16–18], Mg [19], and Zr [20]. To evaluate the strengthening or weakening effect of segregants on GB cohesion, one prevalent approach is to calculate the segregation

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energy difference between a GB and a fracture free surface (FS) using the Rice-Wang model [21]. The embrittling impurities have a stronger binding to the surface than to the GB, with an opposite tendency for GB strengthening elements. This method describes the effect of an impurity on intergranular embrittlement from an energy point of view. Another method is the first-principles computational tensile test (FPCTT): a uniaxial tensile strain is applied in the direction normal to the GB plane via extension of the computational cell by small increments and then all atoms are allowed to fully relax [10,22–24]. The computed total energy and separation distance are used to calculate both the separation energy and the theoretical tensile strength. This method has been successfully applied previously to Ni and Al GBs to understand the impurity-induced GB embrittlement when the fracture plane is set a priori and a pre-crack is introduced at this plane [12,14].

As for the impact of solute segregation upon the GB cohesion in W, few studies were reported up to now, including detrimental elements H, He, N, O, P, S, Li and Si on GB strength, and beneficial elements B and C [25–27]. By investigating the effects of 4*d* and 5*d* transition metals (TM) on the cohesion of Σ27(525) W GB, it was found that lower-valence solutes (Hf, Ta) and higher-valence solutes (Ru, Re, Os) strengthen the cohesion at different sites [28]. Recently, study of Re segregation in highly alloyed W-25 at.% Re has shown that the segregation of Re increases the work of separation for both W and W-Re alloy, which is consistent with the experimental work that an increased tendency for transgranular cleavage in W-Re alloys [29]. However, it is worth noticing that the segregation of solutes and their impact on GB cohesion should be related to the GB structures the solute itself. By now the dependence is poorly understood. Further, no information is reported about the impact of solutes on W GB strength such as fracture energy and tensile strength during stretching. To reveal the dependence of the GB strengthening on the GB structures and the solute itself, the present study is focused on the segregation and strengthening behaviors of transition metal elements (3*d*, 4*d* and 5*d*) in a series of low-Σ symmetric tilt W GBs with [001], [110] and [111] tilt axes. The results reveal that the GB strengthening by solutes in W shows a positive correlation with the metallic radius of solute, and the strengthening effect displays an increasing trend with increasing the GB energy. Moreover, based on the obtained database of solutes segregation and their enhancement on GB strength, we find that the experimentally observed improvement of fracture resistance in W by Re/Ta/Zr impurity is induced by the GB strengthening due to their segregation.

2. Structural models and computational details

Our numerical calculations are performed using density functional theory implemented in the Vienna *ab*-initio simulation package (VASP) code [30,31]. The interaction between ions and electrons is described by the projector augmented wave potential (PAW) method [32]. The exchange and correlation functions are taken in a form proposed by Perdew and Wang within the generalized gradient approximation (GGA) [33,34]. The plane wave cutoff and *k*-point density are both checked for convergence for each system to be within 0.001 eV per atom. The cutoff energy of 500 eV is used in all calculations and the *k*-point mesh given in Table 1. All atoms are relaxed until the forces on each of them are less than 0.001 eV/Å in our calculations. The volume is relaxed for each GB supercell without impurities and then kept fixed when impurities are inserted.

The calculated tilt grain boundaries are constructed using the coincidence site lattice (CSL) model. In this study, to examine the effect of GB structures on the segregation and cohesion behavior of transition metals in W, we construct eight low-Σ symmetric tilt W GBs with [001], [110] and [111] tilt axes, as shown in Fig. 1. The equilibrium structures of the GBs coincide with the experimental observed images of molybdenum GBs and coincide with the GB structures in bcc Fe, as shown by the Supporting material. To eliminated interactions between the two GBs in the supercell, the slabs are separated with 10 Å of vacuum sufficient to exclude interactions between periodic images. The schematic representation of the GB unit cells and the test of the vacuum thickness and GB size are presented in the Supporting material. To get reliable results, the slab needs to be thick enough to render a bulk-like environment in the inner part. The convergence of results for different GBs with regard to their cell sizes is also determined by comparing the site-projected density of states (DOS) of the GB and the bulk supercells. The comparison shows that as one moves away from the GB plane and reaches the sixth layer for Σ5(210), Σ5(310), Σ3(111) and Σ3(112) GBs, and reaches the ninth layer for Σ7(213), Σ9(114), Σ11(323) and Σ13(510) GBs, the DOS of the GB supercell and the bulk supercell matches, i.e., in the centre of the grain, bulk-like conditions are obtained. The data of tilt angles, layers and atom numbers are also summarized in Table 1.

After structural optimization of GBs with segregated solutes, the GBs reveal quite different structural motifs at the interface plane. For Σ3(111), Σ3(112), and Σ5(310) GBs, they holds the mirror symmetry and the geometries are in agreement with previous works on W [25–27,35]. For Σ5(210), Σ13(510), Σ7(213), and Σ11(323) GBs, the structural optimization has shifted the grains with respect to each other in such a way that the GBs have lost their mirror symmetry. The similar phenomena were also observed in other GBs of bcc metals [36–38]. In addition, both of GB sliding and migration occurs for Σ9(114). The characteristics of GB sliding and migration are displayed in Table 1.

The GB energy γ is determined from the difference in energy between the supercell containing GB and another supercell of an equal number of atoms in the bulk environment, divided by the cross-section of the supercell. Therefore, the GB energy γ is given by

$$\gamma = \frac{E_g - E_s}{S}, \tag{1}$$

where E_g is the total energy of the supercell containing GB, E_s is the total energy of an equal number of atoms in the bulk environment, and S is the cross-section area on the xy plane in the supercell. The γ values for different GB structures in this work are shown in Table 1. It can be observed that γ of Σ3(112) has the lowest value of 0.70 J/m^2, which is in good accordance with the previous experimental observations in W GBs [27,39,40] and also in Fe GBs [38,41].

To assess the impact of solutes on the state of GBs, one should firstly investigate their ability to segregate to a GB and secondly determine their effect on the cohesive strength of GBs. The segregation energy is the energy needed for an impurity atom to diffuse from a bulk site to a GB site and can be calculated using

$$E_{seg} = E_{GB}^{X} - E_{Bulk}, \tag{2}$$

whereE_{GB}^{X} is the total energy of the system with a GB and an alloying atom in a site along the GB, and E_{Bulk} is the total energy of the system with a GB and an alloying atom in a bulk site. The site located at approximately equal distances from the GB plane and from the surface of the slab model is chosen as the bulk-like site. Here a negative segregation energy E_{seg} implies that impurity atoms prefer to remain in GBs rather than inside grains, and this situation is opposite for positive E_{seg}. To find the favorable site for the TM solute atom in the GBs, the formation energies of typical alloying elements of Ti, V, Zr, Ru, Ta and Re at interstitial and substitutional