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The nature behind the preferentially embrittling effect of impurities on the ductility of tungsten

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ABSTRACT

It is well known that the ductility of tungsten is very sensitive to impurities while the ductility of tantalum is tolerant to them. However, the fundamental reason behind this preferential effect still remains elusive. Here, based on first-principles calculations, we demonstrated that impurities in tungsten are more likely to segregate into the investigated grain boundary region and the vicinity of straight screw dislocation core than in tantalum, thus having more chances to decrease the ductility. In turn, the presence of impurities, if deemed undesirable, will cause a greater reduction in the grain boundary separation energy for tungsten. The analyses of the chemical and mechanical effects of impurities based on an elegant model suggest that, for the deleterious impurities that have similar binding behavior with tantalum and tungsten, if their effect is repulsive at all relevant site, tungsten is more sensitive to them due to its low lattice constant and high elastic modulus despite other possible causes.

1. Introduction

Tungsten and tantalum are neighbors in the Periodic Table of the Elements and they share many common properties such as high cohesive energy, high melting point (refractory), high mass density, and body-centered cubic (BCC) lattice structure. Their mechanical properties, however, are rather different. Tantalum is much more ductile than tungsten; whereas tungsten is much stronger than tantalum. Further, the ductility of tantalum is tolerant to impurities [1]; whereas the ductility of tungsten is very sensitive to them [2]. From high to commercial purity, the corresponding increase of the ductile-to-brittle transition temperature (DBTT) for tantalum is only about 20 K [1,3]; in sharp contrast, the increase of DBTT of tungsten is more than 400 K [4–6]. In tension, at room temperature, commercial purity tungsten even behaves like a completely brittle material [7]. As a consequence, the applications of commercial purity tungsten have been greatly limited due to its high DBTT and brittleness.

For polycrystalline materials, ductility is determined by the competition between the separation of grain boundaries (GBs) and dislocation activities. Materials with weak GBs and/or low dislocation mobility tend to be brittle; in contrast, materials with strong GBs and/or high dislocation mobility tend to be ductile. The effect of impurities on the ductility of materials manifests itself on the ease of GB separation and dislocation activity. Weakening the GBs and/or decreasing the dislocation mobility can decrease the ductility. Based on this understanding, many efforts have been undertaken to investigate the brittleness of commercial purity tungsten and most of them attributed it to the weakened GBs by the segregated impurities. Hydrogen, O, Si, P, and S etc. weaken the GBs of tungsten, whereas a few impurities such as B and C enhance them [8,9]. When distributed around the dislocation core in tungsten, the impurities can retard the dislocation movement [9] or increase the activation energy of dislocation movement [2], thus decreasing the ductility or increasing the DBTT.

It is worth noting that segregated impurities have a similar effect on the GBs and dislocations of tantalum. When segregated into the GB region of tantalum, O, Si, P, and S etc. weaken the GBs, whereas B and C enhance them [10]. Impurities can also increase the hardness of tantalum by pinning the dislocations [11]. Here lies the question: since impurities influence both metals, why does the ductility of tungsten suffer much more from their deleterious effects, while that of tantalum is more tolerant to them? Due to its greater sensitivity to impurities, much of the published literature concentrated on their effect on the ductility of tungsten. In contrast, considerably less work has been performed

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on tantalum. With regard to the impurity effect on ductility, the literature concentrated more on the role of GBs [12–15], but less on the effect of dislocations. In addition, the literature concentrated more on the influence of properties of the impurity, but less on the influence of properties of the matrix material. Therefore, the understanding of why and how impurities affect the ductility of these refractory metals are incomplete and the nature behind the preferentially embrittling effect of impurities on their ductility, especially that of tungsten, still remains elusive despite ample experimental evidences and theoretical investigations.

Here we made a comparative study of the effect of impurities on the ductility of tantalum and tungsten with first principles calculations based on density functional theory (DFT). We investigated the effect of impurities on both the GBs and dislocations, and systematically calculated the GB segregation energy, dislocation core segregation energy, and the reduction of GB separation energy of various impurities (H, B, C, N, O, F, Al, Si, P, S, and Cl) in both metals. The results show that the synergy of impurity effects on the investigated GBs and dislocations renders the ductility of tungsten to suffer much more from the impurities. Based on our theoretical model that entails both the impurity and matrix properties, we proved that, for the impurities that have similar binding behavior with tantalum and tungsten, the ductility of tungsten is more sensitive to them due to its low lattice constant and high elastic modulus.

2. Methodology

2.1. Atomic configurations

To make the comparison, identical atomic configurations and corresponding impurity sites were used to do the relevant calculations for both tantalum and tungsten. A $\sum 3(1\,1\,1)$ symmetric tilt GB (Fig. 1) was used to calculate the GB segregation energy and reduction of GB separation energy induced by an impurity. A single crystal configuration (Fig. S1) was used to calculate the impurity binding energy in a bulk site. The chosen impurity site have the largest volume in both GB and bulk site, which are highly possible to be the lowest energy location for impurity atom if the impurity has repulsive effect on the matrix, since larger site volume means lower potential energy. The atomic configuration used to calculate the impurity binding energy in a free surface (FS) site is shown in Fig. S2, where the contaminated FS can be considered as a consequence of separation of the contaminated GB, and the location of the impurity atom at the FS is identical to that at the GB before separation.

The dislocation core segregation energy is calculated using a straight screw dislocation model as shown in Fig. 2. To take care of the long-range displacement field of the screw dislocation, we first created a large single crystal slab as shown in Fig. S3, then we displaced all the atoms in z direction according to the displacement field of a screw dislocation determined by the theory of elasticity. The displaced configuration was further equilibrated with conjugate gradient method using empirical potentials [16,17]. Then a monoclinic super cell (red and green atoms) was taken out as the starting configuration in first principles calculations. The size of the monoclinic cell in x and y direction is the same as that used in Ventelon's work [18]. They have shown that this size is large enough to calculate the Peierls energy. The size in z direction is four times that in Ventelon's work, in order to avoid strong interactions between impurities through periodic effect especially in z direction. The geometry of the taken configuration was further optimized using first principles calculations, where the outmost atoms (red) were fixed. The screw dislocation is right handed and has an easy core structure, which is more stable than a hard one [19]. At equilibrium, the clean dislocation core of both tantalum and tungsten shows a symmetric structure, consistent with the literature work of BCC metals [18,20,21]. The white spot indicates the position of an interstitial impurity atom. Our pilot calculations have shown that the center of the screw dislocation core is not a stable site for the impurity atom and eventually pushes the impurity atom into its vicinity site shown by the white spot.

In order for the impurities to affect the GBs and/or dislocations, first they must segregate into the corresponding region. The probability of segregation of impurities into the GB or dislocation core region is determined by the GB or dislocation core segregation energy. Or more precisely, it is defined as the binding energy difference of each impurity atom with the matrix material between a bulk site and GB/dislocation core site, i.e.,

$$\Delta\mu_{GB} = \mu_{GB} - \mu_{BULK}$$
$$\Delta\mu_{CORE} = \mu_{CORE} - \mu_{BULK}$$

where μ_{GB}, μ_{CORE}, and μ_{BULK} are the binding energies of an impurity atom within the matrix when located at a GB, dislocation core, or bulk site, respectively. The embrittling effect of impurities at a GB site is determined by the reduction of GB separation energy [22]

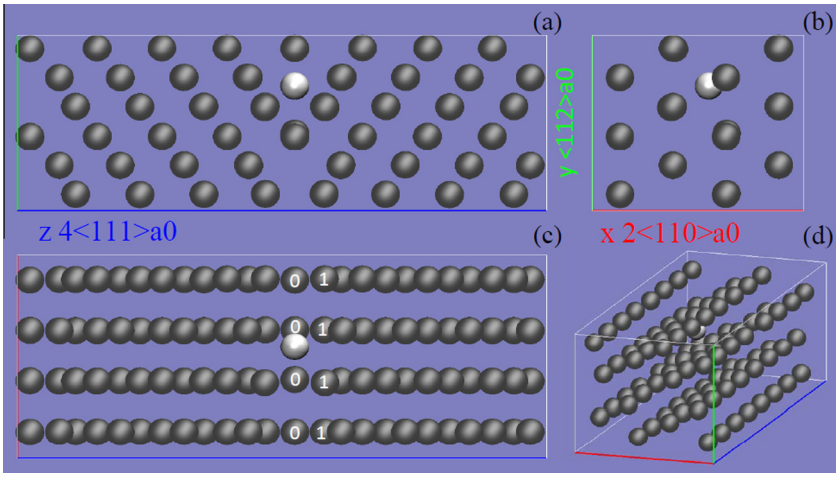

Fig. 1. Standard views of the atomic configuration of $\sum 3\,(1\,1\,1)$ symmetric tilt grain boundary (STGB). The white atom is the interstitial impurity atom inside the GB, which can be removed to calculate the GB energy without impurity atom. The super cell contains 96 matrix atoms and one impurity atom. Periodic boundary conditions are applied in all three directions.