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Intergranular fracture of tungsten containing phosphorus impurities: A first principles investigation

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ABSTRACT

In the present work we have studied the influence of phosphorus impurities on the grain boundary strength of tungsten by means of quantum mechanical calculations based on density functional theory. As model grain boundary we consider the $\Sigma5(3\,1\,0)[0\,0\,1]$ high angle configuration. The results show that by the introduction of a clean (i.e. impurity free) grain boundary in the bulk, the strength and peak stress of the cohesive zone are reduced and they are further reduced by the introduction of impurities. This effect can be attributed to the formation of polar bonds between W and P, which leads to a weakening of the interface. Based on a thermodynamic analysis of the cohesive zone during the straining we find that diffusion of impurities may occur to retain thermodynamic equilibrium for constant chemical potential. This contributes to the gradual reduction of the peak stress related to fracture, which can contribute to diffusion driven delayed cracking, even when subjected to static loads.

1. Introduction

Owing to its high melting point, low coefficient of thermal expansion, high thermal conductivity and sputtering resistance, tungsten (W) and its alloys are considered to be the leading solid material candidates for plasma-facing components in future fusion devices such as the Tokamak reactors in the international thermonuclear experimental reactor (ITER) as well as the planned future demonstration fusion reactor (DEMO). Much of these attractive features emanate from the strong bonding between 5*d* electrons, which results in remarkably high cohesive energy (~ 8.9 eV/atom [1]). However, a fundamental concern of using W for such applications is the high ductile to brittle transition temperature (DBTT) and its dependence on the microstructure and impurity concentrations [2–6]. Experiments have revealed that the DBTT for single-crystalline tungsten can be as low as −196 °C [7], whereas poly-crystalline samples can remain brittle up to about 800 °C [8]. For the application of fusion reactor components, this is a major concern in light of the fact that the temperature at the armour material of the first wall and diverter under operating conditions typically lie in the range ~600–900 °C, which in principle means that the first wall armour material is at risk of rupturing because of brittle fracture [2,9,10]. This is of particular importance for the thin layer tungsten diverter surface, which is subjected to significant thermal gradients, resulting in stresses that can reach hundreds of MPa at regular operation and even higher stresses when subjected to transient loads such as plasma disruptions [9,10].

To explain the wide range of DBTT, a number of experimental studies have been performed to bring insight on the mechanisms responsible for its behaviour. It has been deduced that the DBTT is strain rate dependent and there is a strong correlation with the activation energy associated with screw dislocation mobility. Moreover, the introduction of impurities increases the activation energy, implying further reduced dislocation mobility for impure tungsten which is attributed to impurity segregation at the dislocation core inhibiting the movement [11,12]. The DBTT is expected to be further increased while in operation, because of the cascade damage following the unprecedented degree of radiation that the material will be subjected to during operation. Moreover, transmutation of tungsten into rhenium or osmium may contribute to precipitation hardening [13]. These events collectively will result in a change in the microstructure with increased vacancy, self-interstitial and dislocation densities along with formed precipitates that further reduce the ductility and inhibits dislocation movement [2].

Because of the high melting temperature (~3400 °C [1]), tungsten products are commonly fabricated through the employment of powder technology, rather than melting or casting. Thus, most tungsten materials for practical applications have a poly-crystalline microstructure. To gain insight on the fracture

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behaviour of poly-crystalline tungsten, experimental studies have been performed to compare the fracture behaviour of single- and technically pure poly-crystals [12,14]. These works have shown that cleavage failure along the grain boundaries limits the fracture toughness in poly-crystalline W and the explanation commonly cited is that segregation of impurities at grain boundaries reduces the grain boundary strength and results in mode I type cleavage as opposed to ductile failure. In particular, it has been believed the main cause of this behaviour can be attributed to impurities of sulphur (S), oxygen (O) and phosphorus (P) segregated at the grain boundaries, whereas carbon (C) and boron (B) impurities improves the strength [2]. Of these elements, especially P has been deemed to be the main culprit of the grain boundary embrittlement of technically pure tungsten. This conjecture has been motivated by an observed correlation between loss in ductility and increasing P content [15]. However, recent experimental works have indicated that impurity free grain boundaries also may preferentially rupture by cleavage [16]. Thus, there are contradicting experimental observations, which could imply that even impurity-free grain boundaries may undergo brittle failure. Therefore the mechanisms responsible for promoting grain boundary cleavage are not fully understood and the degree to which different element impurities weaken the grain boundaries remains elusive. Also the question of whether all the aforementioned impurities affect the grain boundary strength is unanswered, which merits further investigation.

To gain insight on the effect of impurities on the physical and mechanical properties of materials, *ab initio* methods such as quantum mechanical density functional theory (DFT) serve as useful tools to predict the behaviour. Such modelling can be used to predict ideal fracture mechanical properties related to transgranular and intergranular fracture, cf. for instance [17–21] and the references therein. For modelling grain boundary cohesion of body-centered-cubic (BCC) metals, owing to its industrial importance, iron grain boundaries have been the scope of numerous *ab initio* modelling efforts [22–28] to understand the influence of impurities and alloying elements on the grain boundary properties. Although not studied to the extent as to iron, because their electronic structures differs substantially from iron, impurity inhabited grain boundaries in molybdenum [29–31] and niobium [30,31] have been modelled by means of DFT to elucidate how the electronic structure affects the grain boundary cohesion.

With respect to tungsten, works addressing impurity embrittlement were performed by Krasko and co-workers [32,33], who studied the influence of impurities (N, O, P, S, Si, B, and C) on the cohesion of $\Sigma3(1\,1\,1)$ type grain boundaries. It was reported that, with the exception B and C, all considered impurities contribute to a weakening of the grain boundary. Boron and carbon, however, were found to improve the grain boundary cohesion. In light of the potential application of tungsten as plasma-facing material, recently some studies have been conducted to investigate the embrittling potency of impurities by means of DFT modelling in conjunction with the ideal grain boundary fracture energy criterion formulated by Rice and Wang [34]. For these applications H and He isotopes are of particular interest, which based on the Rice-Wang criterion have been found to reduce the grain boundary fracture energy [35,36]. Moreover, it has been predicted that H-impurities lower the peak stress required for decohesion [35]. Similar modelling has been employed to identify potential transition metal candidates to improve the grain boundary strength [37–39]. Such works have revealed that solutes located at the centre of the *d*-band in the periodic system are beneficial for improving the grain boundary strength [39]. Regarding P impurities in W, based on the Rice-Wang formalism it has been observed that the introduction of impurities leads to grain boundary weakening [40]. Moreover, by separating the mechanical and chemical effects, a recent DFT-based work [41] has implied that the small lattice parameter and the strong bonding of tungsten yield an enhanced embrittelling effect when impurities are introduced, compared to other BCC metals.

Despite that previous DFT-based works, in accordance with experimental results, have established that P impurities lead to an embrittlement of tungsten grain boundaries - detailed investigation of the gradual reduction in grain boundary strength during the separation and the cleavage behaviour remains. Thus, the purpose of the present work is to study the influence of P impurities on the grain boundary strength by means of DFT modelling. In particular, we aim to investigate how they affect the peak stress associated with decohesion and Griffith work of fracture, and how the impurity transport influences the cohesive strength during the mode I opening based on a thermodynamic description of the equilibrium impurity coverage. This will give qualitative insight to the influence of P atoms on the cohesive strength of grain boundaries and provide traction-separation data that can be used for macroscopic cohesive zone modelling of intergranular fracture in tungsten. Moreover, as part of this work we investigate how the charge distribution is altered by the addition of P-impurities in the grain boundary, to study the electronic mechanisms behind the impurity induced grain boundary weakening.

The paper is organised as follows: In the following section, continuum modelling of brittle fracture and decohesion are discussed. This is followed by a description of the computational methods used in this paper and a disposition of the obtained results. Finally, the paper ends with a short summary of the observations and conclusions.

2. Cohesive zone modelling of cleavage fracture of grain boundaries

For fracture events displaying limited plasticity the cohesive zone approach is a useful tool for modelling the interfacial energetics and traction-separation behaviour in the process zone [42,43]. The total response of the solid can be described in terms of the cohesive zone model representing the interfacial strength and the elastic response of the underlying atomic planes. To extract the cohesive zone parameters based on first-principles modelling it is necessary to assume that the inclination between the decohering planes is small such that the crack opening can be described by the separation of essentially parallel planes. For the case of brittle decohesion this is a good approximation in the local proximity of the decohering site and gives insight to the fracture properties of the material.

For modelling brittle fracture of grain boundaries in solids, it is beneficial to consider the interface as a cohesive zone embedded in an elastic medium. This encourages the employment of excess properties such as proposed by Gibbs for describing interfaces [44–47]. Through this approach the excess properties can be used to represent inhomogeneities such as interfaces and grain boundaries in the material. The excess energy of a decohering grain boundary can be defined as the difference between the total energy of the fracturing solid and that of an ideal bulk. This definition suggests that the surrounding crystalline regions retain bulk properties and that the fracture is localised at the interface. The excess energy is described by a potential $\phi(\delta,\theta)$ that gives the strain energy in terms of the interplanar separation, δ, and the impurity coverage, θ.

Owing to the fact that impurities may be attracted to regions of high stresses, it may be necessary to account for impurity diffusion towards the crack tip when computing the cohesive zone properties. Such diffusion leads to varying degrees of impurity coverage for the gradually separating crack surfaces and it can occur either