Fracture, Damage and Structural Health Monitoring

Simulation of mechanical effects of hydrogen in bicrystalline Cu using DFT and bond order potentials

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Abstract

Hydrogen embrittlement is a prime cause of several degradation effects in metals. Since grain boundaries (GBs) act efficiently as sinks for hydrogen atoms, H is thought to segregate in these regions, affecting the local formation of dislocations. However, it remains unclear at which concentrations H begins to play any role in the mechanical properties of Cu. In the current study, we use density functional theory (DFT) to assess the accuracy of a bond order potential (BOP) in simulating the segregation of H in Cu Σ5 GB. BOP accurately predicts the most favorable segregation sites of H in Cu GB, along with the induced lattice relaxation effects. H is found to weaken the crystal by reducing the GB separation energy. Classical molecular dynamics (MD) simulations using BOP are performed to evaluate the concentration of H in bicrystalline Cu required to substantially impact the crystal's mechanical strength. For concentrations higher than 10 mass ppm, H significantly reduces the yield strength of bicrystalline Cu samples during uniaxial tensile strain application. This effect was attributed to the fact that H interstitials within the GB promoted the formation of partial dislocations.

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1. Introduction

Hydrogen is known to degrade the mechanical performance of metals (Troiano (1960)), a phenomenon referred to as H embrittlement. Though the impact of H embrittlement on performance of electronic devices and industrial components is known to be detrimental, the exact mechanism of this effect is not fully understood (Louthan (2008); Djukic et al. (2016); Li et al. (2019)). The origin of various complex defects, such as voids and cracks, which have been shown to initiate at grain boundaries (GBs) of polycrystalline metals (Moser et al. (2021); Konishi et al. (2002)) is often associated with the presence of non-metallic impurities, such as H (Yamaguchi et al. (2019)), which tend to

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segregate at these regions (Lousada and Korzhavyy (2022)). Once introduced in the GBs, H interstitials can have a stabilizing effect on metal vacancies (Fotopoulos et al. (2023b)), facilitating the initiation of voids. Apart from GBs, dislocations are also known to act as trapping centers for H (Wan et al. (2019); Lynch (2012)). The absorption of H atoms by either dislocations or grain boundaries can promote corrosion and loss of ductility via weakening of metal-metal bonds (Birnbaum and Sofronis (1994); Robertson (2001)).

Electrochemically deposited (ECD) Cu films are commonly used as an interconnect in electronic devices, which operate at elevated temperatures or under high-stress conditions (Needleman (1987)). H is introduced during the deposition through aqueous electrolytes (Gabe (1997)). Once introduced, atomic H can diffuse through the film, getting trapped and aggregating in defects (Li et al. (2020)). Compared to other metals, such as Ni and Pd (Wipf (1997)), the amount of incorporated H in Cu is significantly lower (Fotopoulos et al. (2023a)). Thus the amount of H required to significantly impact the mechanical properties of Cu is unclear. This can be elucidated via theoretical simulations.

Simulating the mechanical properties of polycrystalline metals using atomistic methods requires large scale models, beyond those attainable to ab initio approaches (Yoo et al. (2021)). Therefore many previous studies employed empirical potentials to model metallic systems under external strain (Wang et al. (2013)). Bond order potentials (BOPs) have been shown to accurately predict bulk properties of not only pure metals but also of various Cu (Zhou et al. (2015)) and Al hydrides (Zhou et al. (2018)). However, the properties of H interstitials in Cu GBs along with the induced relaxation effects obtained via such potentials have not yet been compared with DFT results. Therefore, how accurately BOP can predict the properties of individual H atoms in Cu GBs remains unclear.

Here we provide a more in-depth investigation into the mechanical effect of H in bicrystalline Cu. Comparison between the density functional theory (DFT) and BOP calculations demonstrates that BOP can accurately predict favorable segregation sites and the lattice relaxation induced by H in Cu Σ5 GB. Our DFT results show that the presence of H increases the separation energy of Cu GB. The latter is attributed to the induced strong lattice relaxation and significant charge redistribution due to the presence of H. Moreover, H in bicrystalline Cu is found to reduce the yield strength of the crystal at all tested concentrations, however, for a substantial reduction, a minimum of 10 mass ppm of interstitial H atoms in the GB is required. These effects are attributed to the fact that H promotes the emission of partial and Shockley dislocations from the grain boundaries during uniaxial tensile strain application.

The paper is organized as follows. In section 2, the computational parameters of our static calculations using DFT and BOP are outlined along with the technical details of BOP MD simulations. In Section 3.1, we compare the DFT and BOP static results of H in small Cu GB systems. Our ab initio results showcasing the role of H in Cu GB under strain are presented in Section 3.2. In Section 3.3, the impact of different concentrations of H atoms on the mechanical strength of larger bicrystalline Cu models under tensile strain is presented. Finally, the main conclusions are summarized in Section 4.

2. Methods

2.1. Bond Order Potentials

BOPs differ from empirical force fields, such as the embedded atom method (EAM) potentials, in that the covalent bonding and charge transfer are contained within the expansion of the total energy. Thus, BOPs can be applicable to a wide range of materials and types of bonding. BOPs are derived from DFT via the simplification that the tight-binding (TB) approximation provides (Drautz et al. (2015); Silver et al. (1996); Voter et al. (1996); Drautz et al. (2015)) and allow us to model the Cu–Cu, Cu–H and H–H interactions. For the Cu–H interactions, crucial is the accurate description of σ bonding. π bonding is not included and the potential uses as a basis the potentials developed by Pettifor and Tersoff (Oleink and Pettifor (1999)), which are considered to describe accurately the σ bonding between metals and hydrogen atoms (Zhou et al. (2015); Justlin et al. (2005); Zhou et al. (2018)). It is important to emphasize here that these potentials have been developed to accurately describe the growth of Cu in a H-rich environment. Thus, since in our case the goal is to investigate the H segregation in bicrystalline Cu, comparison with DFT results is needed.
2.2. Computational Details: First Principles

Static DFT calculations are carried out for 76-atom (GB; 7.27 Å×8.13 Å×24.39 Å cell dimensions) and 108-atom (bulk; 10.86 Å×10.86 Å×10.86 Å cell dimensions) periodic simulation cells. The Vienna Ab Initio Simulation Package (VASP) (Kresse and Hafner (1993); Kresse and Furthmüller (1996a,b)) and the Perdew–Burke–Ernzerhof (PBE) GGA functional (Perdew et al. (1996)) are used. In line with previous studies in Cu (Ganchenková et al. (2014)), a mixture of the Davidson (1975) and RMM-DIIS (Pulay (1980); Wood and Zunger (1985)) algorithms are used to minimize the energy with an energy tolerance of 10−5 eV. We consider the (210)[100] Σ5 twin boundary (see Figure 1(a)(i)), which is one of the lowest energy grain boundaries in Cu (Wu et al. (2016)). The simulation cell is periodically translated in the x, y, and z directions. Along the z direction, a 10 Å vacuum is added in order to avoid interactions between periodically translated images. For the 76-atom GB and the 108-atom bulk cells, in line with previous works (Nazarov et al. (2012, 2014); Bodlos et al. (2022)), converged 5×4×1 and 4×4×4 k-point grids are used, respectively, with an energy cutoff of 450 eV. In the case of the GB cells, due to the added vacuum, 1 k-point is used along the z direction. The Cu pseudopotential with 11 valence electrons (3d104s1) is used in all calculations.

2.3. Computational Details: Bond Order Potentials

All BOP simulations are conducted using the Large-scale Atomic Molecular Massively Parallel Simulator (LAMMPS) code (Thompson et al. (2022)). Geometry optimization is performed using the conjugate gradient (CG) algorithm with a force tolerance of 10−10 eV/Å. A further equilibration process is followed under an isothermal-isobaric NPT ensemble while retaining a constant temperature of 0 K for 0.02 ns. A timestep of 1 fs is chosen for all MD simulations. For our uniaxial tensile strain simulations, a periodic in all 3 directions 8.1 nm×24.3 nm×3.6 nm (210)[100] Σ5 120,000-atom grain boundary cell is used. H interstitial atoms are introduced in the grain boundary region of the bicrystalline simulation cell at concentrations ranging from 10 to 40 mass ppm. The mentioned concentrations are within the reported experimental range (Fukai (2003); Fukumuro et al. (2011)).

During tensile loading, uniaxial tensile deformations are introduced along the y-axis at a constant strain rate of 10⁸ s⁻¹ and a constant temperature of 300 K, in line with previous MD studies in Cu (Zhao et al. (2016); Zhou et al. (2017)). During the simulations, the x and z-direction boundaries are allowed to vary to maintain the corresponding components of the stress equal to zero by using the isobaric-isothermal NPT ensemble. For determining the atomic positions and velocities, the Verlet numerical integration algorithm is used (Kapoor and Nemat-Nasser (1998)). The formed dislocations are identified using the dislocation extraction algorithm (DXA) (Stukowski et al. (2012)). The common neighbor analysis (CNA) is used for the structural analysis.

2.4. Energetic Parameters

Segregation energies indicate whether H prefers to sit at grain boundaries or in the bulk. In order to calculate the segregation energies of H in Cu GB, four interstitial sites are tested (see Figure 1(a)(i)). The selection of sites is based on previous DFT segregation studies in Cu GBs (Razumovskiy et al. (2018); Wurmshuber et al. (2022)). Two interstitial sites in the bulk of bulk Cu are used as a reference with Figures 1(a)(ii) and (iii) showing the tested octahedral and tetrahedral sites in the bulk, respectively. The segregation energies are computed using the following formula:

\[ E_{seg} = (E_{GB+H} - E_{GB}) - (E_{Bulk+H} - E_{Bulk}), \]  

where \( E_{Bulk+H} \) and \( E_{GB+H} \) are the minimized total energies of the 108-atom bulk and 76-atom grain boundary Cu cells, respectively, containing one H interstitial atom. \( E_{Bulk} \) and \( E_{GB} \) are the respective H-free bulk and grain boundary energies. Negative energies correspond to favorable GB segregation.

The impact of impurities on the grain boundary strength can be measured by the strengthening energy (\( E_{str} \)) based on the Rice-Wang (Rice and Wang (1989)) model:

\[ E_{str} = (E_{GB+H} - E_{GB}) - (E_{Surf+H} - E_{Surf}), \]
where $E_{\text{Surf}}$ and $E_{\text{Surf}+\text{H}}$ are the total energies of the H-free Cu free surface and free surface with one H atom. For surface simulations, a $3\times3\times3$ 108-atom (100) simulation cell is used with an extended z dimension (added vacuum), having a thickness of 10.86 Å. H atoms are introduced at the hollow sites of the surface. A negative value of strengthening energy means that the impurity will enhance the grain boundary strength, while a positive value suggests weakening effect.

For the DFT tensile strain simulations, we employ the approach proposed by Yamaguchi et al. (2005). Based on the latter, a fracture plane is chosen in advance, and the pre-crack is introduced along this plane as the separation between the two grains is increased. Then, the separation energies are simply computed as the difference between the total energy of the GB cell at a specific separation between the two grains and the total energy of the GB cell at the equilibrium separation. The choice of the fracture plane is based on previous DFT studies of embrittlement effects in Fe (Scheiber et al. (2020)).

3. Results

3.1. Comparison of DFT and BOP calculations

One of the goals of this study is to compare the DFT findings to those obtained using BOP. The main energetic properties that we are interested in are the segregation and strengthening energies of H in Cu GB along with the induced lattice relaxation effects. Figure 1 summarizes the segregation results for H in Cu GB obtained using DFT and BOP. The comparison of the segregation energies of H between the two methods for all examined interstitial sites is shown in Figure 1(b). H prefers to segregate as an interstitial atom instead of substitutional, with the octahedral interstitial position being the most favorable in the bulk. The octahedral interstitial site is more favorable compared to the tetrahedral one using DFT and BOP by 0.32 and 0.2 eV, respectively. As seen in Figure 1(b), both DFT and BOP identify interstitial site 2 as the most favorable segregation site. The two methods give segregation energies within 0.26 eV difference. All interstitial sites show negative segregation energies (favorable GB segregation).

The two methods are also in good agreement regarding the strengthening energy (Figure 1(b)). In all four tested interstitial segregation sites, H is found to be more favorable to segregate in a hollow site of the (100) surface instead of any of the four examined interstitial sites in the Σ5 GB (positive strengthening energy). This indicates that the presence of H in the GBs will cause local decohesion, since it will facilitate the formation of a free surface in between the two grains. BOP and DFT give strengthening energies within 0.4 eV difference, with BOP giving consistently
lower energies. It can be deduced that, although there is a non-negligible discrepancy between the two methods, the computed energies follow a similar pattern at different segregation sites.

Figures 2(a) and (b) illustrate the fully relaxed configuration of H introduced in the most favorable interstitial site (site 2 as seen in Figure 1(a)(i)) using BOP and DFT, respectively. The resulting distances between H and the four neighboring Cu atoms obtained with both methods agree within 5% of Cu’s lattice constant, namely 3.62 Å. Also, Figures 2(b) and (c) illustrate the displacement vectors (yellow arrows) while atoms are colored based on their displacement, using the initial configuration prior to relaxation as a reference. Both DFT and BOP showed that the most significant displacement is that by H atom by approximately 0.8 Å, which during relaxation causes the displacements by around 0.1 Å of the four adjacent Cu atoms.

3.2. Ab initio strain calculations

So far our results suggest that BOP and DFT are broadly in a good agreement. Prior to conducting MD simulations employing BOP, we sought to understand the underlying mechanism behind the observed weakening effect of H when introduced into Cu GB. Figure 3(a) includes the separation energy of the GB with 1 and 4 H atoms occupying the identified most favorable interstitial segregation sites (site 2 as seen in Figure 1(a)(i)). The inset image illustrates the GB simulation cell along with the plane chosen for the separation, shown as a yellow line. The plot includes full relaxation results obtained using DFT. The GB separation is increased up to the point where the grains are separated and a free surface is formed. The results follow the universal binding energy relation (Ferrante et al. (1981)), increasing rapidly at the beginning and at larger distances start reaching an asymptote. At small distances, also referred to as pre-fracture region (Huang et al. (2018)), the rearrangement of atoms heals the separation between the two grains. The difference between the energies of the separated grains and the GB at the equilibrium separation corresponds to the separation energy. It can be seen that, as the number of H atoms in the GB increases, the separation energy is reduced by approximately 0.1–0.3 Jm⁻². A similar reduction in separation energy due to the presence of H has been reported in Ni GBs (Mai et al. (2021)). Also, we expect these effects to increase with the addition of more H atoms, as shown by Yamaguchi et al. (2019) where up to 14 H interstitials in Al GBs led to a constant decrease in the cohesive energy. These results also are in good agreement with the computed strengthening energies shown in Figure 1(b), where the presence of H shows a weakening effect in the GB.
Figures 3(b)(i) and (ii) show the projected density of states (PDOS) of the H atom and the nearest neighboring Cu atom (Cu1 as seen in Figure 4(a)) at the equilibrium separation and a separation of 1.6 Å in the H-segregated GB model, respectively. At the equilibrium separation, hybridization peaks are observed at -9 eV to -7 eV between the Cu1 and H atoms. The hybridization is present in both separations. However, as the separation distance increases, the interaction between Cu1–H orbitals weakens. Figure 4 illustrates the total charge density of the relaxed configurations at three different separations, namely the equilibrium, 1.6 and 2 Å obtained using DFT with one (Figure 4(a)) and four (Figure 4(b)) H interstitials in Cu GB. As can be seen, H reduces the charge density between neighboring Cu atoms. The GB appears to be more prone to separation as the number of H atoms increases. Previous DFT investigations of one H interstitial in the GB of Fe found similar total charge density patterns (Yuasa et al. (2012)). Our results are also in agreement with the mentioned above study in Fe, showing that a single H interstitial relaxes at the center of symmetry of the GB for a separation of 2 Å. The differential charge density (Figure 4(c)) shows that H tends to accumulate electrons, bonding with adjacent Cu atoms as a result of the hybridization of the s H orbital and s/p/d orbitals from the host Cu atoms.

3.3. MD strain calculations

Our results predict that the presence of H in Cu GB can have a significant brittle effect. Hence, it is of interest to understand the mechanical effect of H when introduced in Cu GB along with the concentrations needed for such an effect to be significant. First, we introduce H interstitials at the identified most favorable sites (site 2 as seen in Figure 1(a)(i)) and at various concentrations in the 120,000-atom bicrystalline Σ5 GB simulation cell shown in Figure 5(a) (inset). Once the cells with and without H are fully relaxed and equilibrated, uniaxial tensile strain is applied along the y-axis.

Figure 5(a) shows the effect of H on the mechanical strength of bicrystalline Cu at increasing mass ppm concentrations (10–40 mass ppm). As can be deduced, for any H concentration higher than 10 mass ppm in Cu GB, the yield strength of the crystal is significantly reduced, namely from 8.4 GPa (pure Cu) to 7.3 GPa (Cu with 40 mass ppm H). Figures 5(b)(i)–(iv) illustrate the correlation between formed partial Shockley dislocations and the concentration of
Fig. 4. Total charge distributions obtained using DFT at equilibrium (first column), 1.6 Å (second column), and 2 Å (third column) separations for Cu GB with (a) one interstitial H (b) four interstitial H atoms. (c) Differential charge distribution of four H interstitial in Cu GB at three different separations, namely equilibrium (first column), 1.6 Å (second column), and 2 Å (third column). The GB separation distances are the same as in (a) and (b). Yellow and cyan iso-surfaces (0.01) correspond to electron accumulation and depletion, respectively.

Fig. 5. (a) Stress-strain plots for pure Cu GB and Cu GB with different mass ppm concentrations of interstitial H atoms. Inset image illustrates the 120,000-atom Cu GB simulation cell. Green atoms correspond to fcc symmetry whereas amorphous regions (GB) are shown in white. Uniaxial deformation is applied along the y-axis. (b) Dislocation emission from the GB for (i) pure Cu and Cu with (ii) 10 (iii) 25 (iii) 40 mass ppm of H interstitials. Only atoms with non-fcc symmetry are visualized, with red and white, corresponding to atoms with hcp symmetry and amorphous structure (GB), respectively. Green lines correspond to Shockley dislocations. Visualization is performed using OVITO (Stukowski (2009)).

H. The formation of hcp planes (red atoms in Figure 5(b)) from the GB initiate as Shockley dislocations (green lines as seen in Figure 5(b)). Therefore, it is apparent that the presence of H interstitials in Cu GB increases the density of partial Shockley dislocations. The latter leads to a significant decrease in the yield strength of the bicrystal. A similar increase in the density of dislocations has been observed in previous MD tensile strain calculations in α-Fe (Wan et al. (2019)). However, we should note that the H solubility in Fe (Nazarov et al. (2010)) is considerably higher compared to Cu (Fukai (2003); Fukumuro et al. (2011)). Therefore, obtaining such H concentrations in ECD Cu is unlikely.
4. Conclusions

We conducted DFT and BOP MD simulations to understand the mechanical effect of the inclusion of H interstitials in Cu GB. Using DFT, H was found to reduce the separation energy of Cu $\Sigma$ 5 GB. This effect was attributed to the induced lattice relaxation and local charge redistribution caused by H, which reduced the charge density between neighboring Cu atoms. The latter led to a weakening of the Cu–Cu bonds close to the H interstitials, causing a local weakening effect.

Compared to the DFT results, BOP accurately predicts the most favorable H segregation sites in Cu GB. Also, BOP calculations are in broadly good agreement with DFT regarding the strengthening energy and local relaxation. Using BOP, H was found to facilitate the emission of Shockley and partial dislocations at the GB. However, at least 10 mass ppm of H was needed for a substantial drop in the yield strength to occur. Further study will be needed to understand the effect of H on the mechanical properties of Cu while taking into account the presence of triple junctions.

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References


