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Hydrogen diffusion and vacancies formation in tungsten: Density Functional Theory calculations and statistical models

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Abstract—The interaction of hydrogen with tungsten is investigated by means of the Density Functional Theory (DFT) and statistical methods based on the transition-state theory and thermodynamics. This model yields temperature-dependent data that can help understanding macro-scale experimental results. Within this model, the concentrations of trapped hydrogen atoms at thermodynamic equilibrium are established. Taking into account the configurational entropy, hydrogen is shown to induce vacancy formation below 1000 K. Based on this model, TDS spectra are simulated with a basic kinetic model to provide some better insight into the desorption process of hydrogen. Finally, revised mechanisms for hydrogen diffusion in tungsten are proposed; we conclude that the discrepancy existing between the experimental diffusion coefficient measured by Frauenfelder (1969) and the one calculated by DFT would be reconciled provided one uses two different diffusion regimes that would depend on temperature and vacancies concentration.

Keywords: DFT; Tungsten; Hydrogen; Vacancies; Nuclear material

1. Introduction

The interaction of hydrogen with tungsten is herein investigated by means of the Density Functional Theory (DFT). Because DFT is limited to small models of about one hundred atoms at zero temperature, this work is complemented by a statistical approach based on the transition-state theory and thermodynamics. This model yields temperature-dependent results that can help understand macro-scale thermodynamics and kinetic experimental data with no need for multi-scale approaches in between. Nevertheless, multi-scale approaches allow predicting tungsten behavior under various physical conditions. As a consequence, these data are also to be integrated in codes like the Kinetic Monte-Carlo [1] and/or Macroscopic Rate Equations simulations [2,3] for example.

Tungsten exhibits many exceptional properties such as extreme hardness (7.5) and the highest melting point in the periodic table of the elements (3683 K) [4,5]. In part because of these properties, tungsten is currently massively investigated for its potential application as a plasma-facing component in the International Thermonuclear Experimental Reactor (ITER) [6,7]. Apart from ITER, and more generally, hydrogen in metals has long been investigated for fundamental and applicative purposes as well. More specifically, hydrogen has the ability to facilitate vacancy formation in metals [8,9], known as superabundant vacancies (SAV) when such vacancies are formed at high concentration. Discovered at the beginning of the nineties, SAVs were first observed in palladium and nickel with concentrations as high as at.20% [10–12]. As vacancies in tungsten are known to trap up to 12 H atoms [13], SAVs are expected to have a significant impact on hydrogen solubility. Hydrogen is also known to have a critical effect on metal embrittlement [14,15] for which vacancy formation induced by hydrogen would be the determinative mechanism [9,16].

However, not all metals can bring about SAVs. In particular, group-VI transition metals like molybdenum and tungsten are known for their low solubility toward hydrogen [13], which is another sought-after property for ITER. Despite its low solubility, hydrogen in tungsten could have an impact on the brittle-to-ductile transition temperature [17]. Hydrogen is also known to induce bubble formation under high fluxes [18,19], which here again is induced by vacancy-assisted mechanisms [20–23]. Hence, understanding of this mechanism has attracted much attention during the last decade, and many DFT-based investigations were conducted about hydrogen diffusion [22,24–26], solubility [25,27,28] and interaction with vacancies in tungsten [23,29–35].

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Comparison with experiment is not straightforward however, since experimental results would appear to deviate from one another. This fact was well documented in a recent review on hydrogen retention by Tanabe [36] and Causey [5]. On the other hand, experimental results are not the only ones to suffer discrepancies; theoretical results also do, and this would be worth looking into. Indeed, in a multi-scale approach, data may need tuning in order to compensate for DFT deviations. Defining error bars would allow tuning DFT data in a well-controlled manner so that multi-scale simulations may come in closer agreement with known experimental results. As a consequence, the first step in this work is to analyze the source of deviations in DFT results and to define error bars. Then, DFT data are included in a statistical model based on the transition-state theory and thermodynamics. The trapping of multiple hydrogen atoms in tungsten vacancies is investigated taking into account the configurational entropy; in this model, hydrogen is shown to induce vacancy formation in tungsten below 1000 K. Using a basic kinetic model, TDS spectra are simulated in order to understand the desorption process. Despite the simplicity of the model, results exhibit a reasonably good agreement with experimental results recorded on single crystalline samples [37,38]. Finally, the diffusion mechanism of hydrogen in tungsten is revised and two diffusion regimes are assumed; they depend upon temperature and vacancy concentration and allow reconciling the activation barrier calculated by DFT and the one measured experimentally by Frauenfelder [39].

2. Methods

2.1. Model

We used working-cells ranging from unity to 4 × 4 × 4 hereafter labeled W1, W2, W3 and W4. Most of the calculations are however performed in a 3 × 3 × 3 supercell (W3) containing 54 atoms. The parameters of the body-centered cubic cell were optimized to $\mathbf{a} = 3.187$ Å at zero pressure and temperature, not far from the experimental value $\mathbf{a}_{\mathrm{exp}} = 3.165$ Å [40] under atmospheric pressure and at room temperature.

2.2. Electronic structure calculations

All the DFT calculations are performed with the *Quantum Espresso* code [41] using the PBE [42] exchange and correlation functional. Some functionals are specifically designed to model surfaces and voids in metals as for example AM05 [43]. In particular, Ventelon et al. [34] and Muzyk et al. [44] have already shown AM05 to produce *a priori* energies for vacancies formation in better agreement than PBE when compared with experimental results at high temperature [45,46]. However, considering temperature and electronic entropy [47], both functionals appear to perform equally well in tungsten [34]. Furthermore, part of the temperature dependence also comes from the vibrational entropy which includes anharmonic lattice vibrations, and which is not currently evaluated. It is therefore not easy to determine which is the most appropriate functional. We currently use the PBE functional, which has already proved to perform well and is widely used for the hydrogen–tungsten system, while keeping in mind that the choice of the functional is probably the main source of discrepancy in the results presented below.

With regard to pseudo-potentials, Middleburgh et al. [29] already showed the impact of using pseudo-potentials with twelve-valence electrons rather than six only as in most studies. The formation energy of a vacancy is reduced to 2.93 eV from 3.32 eV, respectively. Following Middleburgh et al. [29], we include the valence and semi-core electron in the electronic calculation, meaning $5s^2\ 5p^6\ 6s^2\ 5d^4$, for a total of 14 electrons. The scalar-relativistic ultra-soft pseudo-potentials [48] (USPP) were used to model the ionic cores.

Considering the literature devoted to hydrogen in tungsten, a closer look at the methodology section of various DFT papers reveals the use of many different numerical parameters: cutoff of the wave-function for PAW [49] or USPP [48] ranges from 26 Ry (350 eV) to 40 Ry (550 eV) and k-points sampling of the Brillouin zone (reduced to the unit-cell) from 12 × 12 × 12 to 18 × 18 × 18. These parameters are chosen so that the energy of the unit-cell does not deviate more than, let us say 10 meV against some other tighter parameters chosen as the reference. However, such dispersion of parameters could potentially have an impact on some other physical quantities. In this work, these parameters are not only made to converge with respect to the energy of the unit cell, but also with respect to some of the data we intend to calculate. Starting with energy cutoffs as high as 140 Ry (1900 eV) and a k-points sampling of 28 × 28 × 28, looser parameters were then applied in order to reach no more than 1% deviation for (i) the formation energies of mono- and di-vacancies, (ii) the solution energy of hydrogen in a tetrahedral (Td) site, and (iii) the diffusion barrier to reach another Td site. Also considered was the ordering in stability of three different di-vacancies.

We ended up with cutoffs of 40 Ry (544 eV) and 320 Ry (4352 eV) on the wave-function and on the electronic density, respectively. We also converged to k-point samplings from 18 × 18 × 18 to 20 × 20 × 20, i.e. 6 × 6 × 6 for W3 and 5 × 5 × 5 for W4. With such parameters, the deviation is kept below 0.7%, which constitutes an error bar. The most sensitive physical quantity appears to be the formation energy of a vacancy, which can deviate up to 11% with a cutoff of 20 Ry and a k-point sampling of 15 × 15 × 15, i.e. 5 × 5 × 5 for W3.

The vibrational properties are calculated in the formalism of the Density Functional Perturbation Theory [50] as implemented in Quantum Espresso. Due to the mass difference between hydrogen and tungsten, only the vibrational frequencies of hydrogen are taken into account. In order to probe the reliability of this assumption, the vibrational frequencies of an interstitial hydrogen atom were computed in a tetrahedral site at the Γ point. We used the W2 supercell to be able to calculate the entire phonon modes. The full calculation yielded the three following frequencies for H: 1165.8, 1531.2 and 1546.8 expressed in cm^{-1}; the calculation limited to H only yielded 1165.9, 1531.5, and 1547.1 cm^{-1}, which fully verifies the assumption made above.

The temperature dependency of the energies and free energies was also computed. We assumed that energy changes are only due to vibrational properties, thus neglecting the electronic contribution to energy and entropy. This approximation is known to be valid in metals where the vibrational entropy is much higher than the electronic ones [51], even if in the vicinity of vacancies the electronic