



First-principles calculations of hydrogen solution and diffusion in tungsten: Temperature and defect-trapping effects

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Abstract—The solubility and diffusivity of hydrogen in tungsten are fundamental and essential factors in the application of this tungsten as a plasma-facing material, but data are scarce and largely scattered, indicating some important factors might be missed. We perform a series of first-principles calculations to predict the dissolution and diffusion properties of interstitial hydrogen in tungsten and the influence of temperature and the defect-trapping effect. The interstitial hydrogen always prefers the tetrahedral site over the temperature range 300–2700 K, and its migration path mainly advances via the nearest-neighboring tetrahedral sites. Our results reveal that both solution and activation energies are strongly temperature dependent. The predicted solubility and diffusivity show good agreement with the experimental data above 1500 K, but present a large difference below 1500 K, which can be bridged by the trapping effects of vacancies and natural trap sites. The present study reveals a dramatic effect of temperature and defect trapping on the hydrogen solution and diffusion properties in tungsten, and provides a sound explanation for the large scatter in the reported values of hydrogen diffusivity in tungsten.

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1. Introduction

Tungsten is the primary candidate for the plasma-facing material (PFM) of fusion reactors due to its low tritium retention, high melting point, high thermal conductivity and low sputtering yield for light elements [1–4]. In its role as a PFM, tungsten would be subject to high heat and particle flux of hydrogen escaping from the plasma, which would congregate on the tungsten surface or penetrate through it and diffuse deeper into the bulk. Hydrogen retention in tungsten leads to modification of the material's physical and mechanical properties, such as assisting superabundant vacancy formation, inducing embrittlement, and reducing mechanical strength. More importantly, hydrogen retention in PFMs has been identified as a major safety and economic concern in fusion reactors [5]. Thus, the investigation of hydrogen retention in tungsten is an important task for fusion research. To study hydrogen retention in tungsten, knowledge of hydrogen solution and diffusion is fundamental and essential. The solubility and diffusivity play a key role in determining the recombination rate

coefficient and should be directly associated with hydrogen trapping and bubble formation. In addition, they are also used as input in many experimental and computational analyses on recycling and retention of hydrogen in tungsten. Without reliable knowledge of the solubility and diffusivity, reliable predication of hydrogen recycling and retention in tungsten is hardly possible.

Data for hydrogen solubility are scarce. Frauenfelder measured the solubility of hydrogen in 99.95% pure tungsten for the temperature range 1100–2400 K, which was given by $S = 9.3 \times 10^{-3} \exp(-1.04 \text{ eV}/kT) H/(W \text{ atm}^{1/2})$ (here, the solubility S is expressed in terms of the hydrogen/tungsten atomic fraction per square root of the hydrogen pressure on the tungsten in atmospheres) [6]. This agrees well with Mazayev's measured data covering the temperature range 1900–2400 K [7]. The extrapolation of the data to lower temperatures is in fair agreement with Zakharov's [8] (910 K < T < 1060 K) and Ikeda's [9] (298 K < T < 353 K) data evaluated from their diffusivity and permeability data. Although the absolute values of the solubility among these reported data are within the same order of magnitude, their pre-exponential factors and activation energies are completely different. For example, the activation energies are 1.04, 0.03 and 0.19 eV for Frauenfelder [6], Zakharov [8] and Ikeda [9], respectively.

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In addition, Benamati et al. [10] used their permeation data for hydrogen through tungsten with 5% rhenium to approximate the solubility and obtained a constant value ($6 \times 10^{-7} H/(M \text{ atm}^{1/2})$) over a limited temperature range of 850–885 K, which is much higher than the extrapolation of Frauenfelder's data [6] to this temperature range.

As with the solubility of hydrogen in tungsten, data on the diffusion coefficient of hydrogen in tungsten are also very limited. To this end, some experimental studies have been conducted to measure the diffusion coefficient of hydrogen in tungsten. Some earlier investigations on the hydrogen diffusivity at higher temperatures have been carried out by Moore et al. [11] ($D = 7.25 \times 10^{-8} \exp(-1.80 \text{ eV/kT}) \text{ m}^2/\text{s}$, $1200 \text{ K} < T < 2500 \text{ K}$), Ryabchikov [12] ($D = 8.1 \times 10^{-6} \exp(-0.86 \text{ eV/kT}) \text{ m}^2/\text{s}$, $1900 \text{ K} < T < 2400 \text{ K}$), Frauenfelder [6] ($D = 4.1 \times 10^{-7} \exp(-0.39 \text{ eV/kT}) \text{ m}^2/\text{s}$, $1100 \text{ K} < T < 2400 \text{ K}$), Zakharov [8] ($D = 6 \times 10^{-4} \exp(-1.07 \text{ eV/kT}) \text{ m}^2/\text{s}$, $910 \text{ K} < T < 1060 \text{ K}$) and Benamati [10] (about $1.5 \times 10^{-10} \text{ m}^2/\text{s}$, $850 \text{ K} < T < 885 \text{ K}$) based on hydrogen degassing and permeation experiments, which are indirect measurements of hydrogen concentrations. Recently, the hydrogen diffusivity at lower temperatures has been measured by the tritium tracer technique in some experimental works, e.g. Otsuka et al. [13] ($D = 3 \times 10^{-7} \exp(-0.39 \text{ eV/kT}) \text{ m}^2/\text{s}$, $473 \text{ K} < T < 673 \text{ K}$), Ikeda et al. [9] ($D = 3.42 \times 10^{-9} \exp(-0.39 \text{ eV/kT}) \text{ m}^2/\text{s}$, $298 \text{ K} < T < 353 \text{ K}$) and Hoshihira et al. [14] ($D = 4.3 \times 10^{-9} \exp(-0.39 \text{ eV/kT}) \text{ m}^2/\text{s}$, $293 \text{ K} < T < 323 \text{ K}$). Taking literature data at higher temperatures and near room temperature into account, Ikeda and Otsuka [15] proposed a new diffusion coefficient ($D = 3.8 \times 10^{-7} \exp(-0.41 \text{ eV/kT}) \text{ m}^2/\text{s}$) as the most reliable hydrogen diffusivity, which is valuable for a wide temperature range of 250–2500 K.

As summarized above, although various parameters for hydrogen solubility and diffusivity in tungsten have been recommended, few experimental values have been reported and moreover these parameters show large discrepancies. This is particularly true for the values of solution and activation energies. These discrepancies arise from the use of different techniques to obtain the data. In addition, the extremely low solubility of hydrogen in tungsten and the significant surface and trapping effects make the experimental measurements difficult and complex, particularly at low temperatures. At present, it is very hard to give a reliable value for the solubility and diffusivity in tungsten, and data for this is urgently required.

As a result of progress in first-principles computational methods, it is now possible to calculate the solubility and diffusivity of foreign interstitial atoms in metals at a level of accuracy close to and sometimes better than available from experiments; examples include hydrogen and oxygen in nickel [16–18], oxygen in body-centered cubic (bcc) iron [19], carbon in palladium and palladium alloys [20], hydrogen in austenitic high-manganese steels [21], and so on. For these reasons, several researchers have used atomic calculations to investigate the solution and diffusion properties of hydrogen in tungsten. For example, Heinola et al. [22] and Liu et al. [23] have predicted the hydrogen diffusivity in tungsten as $D = 5.2 \times 10^{-8} \exp(-0.21 \text{ eV/kT}) \text{ m}^2/\text{s}$ and $D = 1.57 \times 10^{-7} \exp(-0.19 \text{ eV/kT}) \text{ m}^2/\text{s}$, respectively. These two results are roughly comparable with each other. The slight difference between them may result from the different methods adopted for the jump rate calculation. Unfortunately, both of these diffusivities show large differences from the experimental values, particularly at

low temperatures, suggesting that some important factors might have been missed in these two first-principles calculations.

The temperature effect may be one such omission, as this has been demonstrated to be an important factor for an accurate interpretation of experimental solution and diffusion data using first-principles computational methods [16,18–20], but was not considered in either Heinola et al.'s [22] or Liu et al.'s [23] works. According to the result reported by Dubrovinsky et al. [24], the thermal expansion of tungsten is calculated to be about 1.21%, 2.66% and 4.50% for temperatures of 298, 1205 and 2774 K, respectively. Recent results for the hydrogen behavior in tungsten under hydrostatic strain show that the volume expansion can change the solution and diffusion properties of hydrogen in tungsten [25,26]. Therefore, it can be expected that the temperature effect would affect hydrogen solution and diffusion properties in tungsten. Besides the temperature effect, the defect-trapping effect may also contribute to the large difference of the reported hydrogen solubility and diffusivity data, which has been found to significantly affect the hydrogen solution and diffusion behaviors in metals [27–30]. In tungsten, much work has demonstrated that lattice defects, e.g. vacancies, dislocations, impurities and grain boundaries, can trap multi-hydrogen atoms and impede hydrogen diffusion [31–40]. Until now, the defect-trapping effect has also been used by some researchers to explain discrepancies between the hydrogen diffusivity data in tungsten reported by themselves and by others [10,22]. However, little work has been done to quantify the effect of microstructural defect-trapping on hydrogen transport in tungsten and tungsten alloys.

In this paper, we carry out a systematic first-principles calculation to investigate the temperature and defect-trapping effects on the dissolution and diffusion properties of interstitial hydrogen in tungsten. Here, the temperature effect is taken into account by the thermal expansion and vibration free-energy contribution, and the defect-trapping effect is described through the modified Fick's equation according to Mac-Nabb and Foster [41]. Using the first-principles calculated results, reliable solubility and diffusivity data are predicted according to Sievert's law and transition state theory, respectively. Together with the former reported hydrogen solution and diffusion results, our results reveal a dramatic effect of temperature and defect-trapping on the predicted hydrogen solution and diffusion properties in tungsten, and provide a sound explanation for the large scatter of the above-mentioned data on hydrogen diffusion in tungsten.

2. Computation method

The solution energy is the energy required to place a hydrogen atom at a certain interstitial site ζ in the tungsten. It is defined by:

$$E_{\zeta}^{\text{Sol}} = E^{\text{WH}_{\zeta}} - (E^{\text{W}} + E^{\text{H}}), \quad (1)$$

where $E^{\text{WH}_{\zeta}}$ is the total energy of the tungsten lattice with a single hydrogen atom at site ζ . The reference is given by the total energy per supercell of the perfect tungsten lattice (E^{W}) and the energy of a single hydrogen atom outside the tungsten ($E^{\text{H}} = -3.40 \text{ eV}$, half the energy of a hydrogen molecule, which corresponds to the binding energy of 4.56 eV for a hydrogen molecule, consistent with experimental findings [42]).

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