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Thermodynamic model for grain boundary effects on hydrogen solubility, diffusivity and permeability in poly-crystalline tungsten

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HIGHLIGHTS

- A thermodynamic model to simulate grain boundary effects on hydrogen behaviors in poly-crystalline W was established.
- With this model, the effective solubility, diffusivity and permeability of hydrogen are calculated as a function of grain size.
- Grain boundary significantly change the hydrogen behaviors in poly-crystalline W up to around 1000 K.

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ABSTRACT

A thermodynamic model to evaluate effects of grain boundary (GB) on hydrogen behaviors in poly-crystalline tungsten is established. With this model, the effective solubility, diffusivity and permeability of hydrogen in tungsten equilibrated with surrounding H_2 gas can be calculated as a function of grain size, temperature and H_2 partial pressure. By setting 1.0 eV to the binding energy of hydrogen to GBs and 0.4 eV to the diffusion barrier of hydrogen along GBs, the model reasonably reproduces some experimental data on the effective diffusivity and permeability. Comparisons between calculation results by the model and available experimental data show that GBs significantly affect the hydrogen behaviors up to around 1000 K or higher in practical materials. Therefore, the effects of GBs need to be considered in analysis of experimental results, for which the present model can be utilized, and in prediction of tritium inventory and leakage in fusion reactors.

1. Introduction

Hydrogen solubility, diffusivity, and permeability in tungsten, a promising candidate material for plasma facing components (PFCs) in fusion reactors, are important thermodynamic properties for estimating the tritium inventory and leakage in/through PFCs. Many studies have been performed to evaluate these quantities [1,2]. Hydrogen behaviors in W are not so complicated if the crystal lattice is perfect. In practical materials, however, lattice defects are inevitably involved, and then the solution, diffusion and permeation behaviors of hydrogen largely change. Moreover, in nuclear fusion environment, radiation defects are expected to affect the hydrogen behaviors [3,4].

Lattice defects basically act as hydrogen traps in W, which increase the effective solubility and decrease the effective diffusivity of hydrogen. Many previous studies focused on mono-vacancy and examined its effects on the solution and diffusion behaviors of hydrogen in single-crystal W [5–12]. For example, it was shown that a mono-vacancy traps multiple H atoms in W: up to around 12 H atoms at 0 K [5,9,10] and up to around 6 H atoms at room temperature [9,10].

Dislocation [13], grain boundary (GB) [14–19] and some impurities [2,6,20–22] are also known to act as traps. In experiments on thermal desorption of hydrogen in W, a desorption peak related to intrinsic traps is usually observed. This peak indicates the existence of hydrogen trap to which the binding energy of hydrogen is, for example, 0.85 eV [23] and 0.7–0.9 eV [3] (which is obtained by subtracting a hydrogen diffusion barrier from a detrapping energy). However, it is difficult to assign this peak to a specific defect because several intrinsic traps such as dislocation, GB and impurities are likely to have the binding energies in around that energy range.

Among the lattice defects, GB has been attracting increasing attention due to the importance of GBs in fine-grain W materials [24,25], which are expected to bring improved mechanical properties. Several computational studies were performed to uncover GB effects on the hydrogen behaviors in atomic scale [14–18]. Specifically, two methods of atomistic simulations have been applied to

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study the GB effects. One is first-principles calculation based on density functional theory (DFT), and the other is classical molecular dynamics (MD) method with two bond-order potential (BOP) models parameterized by Juslin et al. [26] and Li et al. [27]. DFT calculation was used to evaluate the stability and the mobility at/around specific GBs, including Σ5 tilt GB [14], Σ3 tilt GB [15] and W(110)/W(112) interface [16], while MD simulation was employed to find general trends of hydrogen stability and mobility in systems containing various types of GBs [17,18].

Despite the accumulation of detailed information on the GB effects thanks to atomistic simulations, the information has not been effectively utilized to interpret and analyze experimental results. One of the reasons of this is that quantities that can be determined by atomistic simulation such as the binding energy of H atom to GB are not simply reflected in quantities that can be obtained by experiment such as effective hydrogen solubility. This is because apparent effects of GBs depend on several parameters including grain size, hydrogen concentration, temperature, etc. In the present study, therefore, in order to systematically relate these two types of quantities, a thermodynamic model is constructed. This model enables us to calculate the effective solubility, diffusivity and permeability of hydrogen in poly-crystalline bcc-W equilibrated with surrounding H_2 gas, as a function of grain size, temperature and partial pressure of H_2 in the gas phase.

The remaining part of the present paper is organized as follows. In Chapter 2, the framework of the thermodynamic model is introduced. The modeling procedure and the definition of model parameters are described. In Chapter 3, calculation results with the thermodynamic model on the effective solubility, diffusivity and permeability of hydrogen are presented with varying grain sizes. The calculation results are compared with available experimental data. In addition, since some model parameters involve non-negligible uncertainties at present, results of sensitivity analyses on such parameters are also provided. In Chapter 4, after discussing uncertainties in the model and model parameters, experimental studies that are expected to contribute to refining the model are suggested and implications to fusion engineering R&D are mentioned. Finally, the paper is closed with concluding remarks in Chapter 5.

2. Methods

In this chapter, first of all, effects of hydrogen traps in general are described in Section 2.1. Then, the scope and the target of the present model is explained in Section 2.2. A thermodynamic model based on the equilibrium theory is derived to achieve the target of the present study in Section 2.3. Model parameters are set in Section 2.4 based on consideration of the structure of poly-crystalline bcc-W and results of reported atomistic simulations. Subsequently, formulation for evaluation of effective hydrogen solubility, diffusivity and permeability is given in Section 2.5. Finally, after summarizing the concept and parameters of the model in Section 2.6, experimental data to compare with calculation results are introduced in Section 2.7.

2.1. Effects of hydrogen traps in general

Each trap has characteristic influence on hydrogen behavior. For hydrogen diffusion, the effective diffusivity (D_{eff}) can be approximated as the weighted sum over contributions of different hydrogen states under the assumption that diffusion between different states do not significantly contribute to D_{eff} [28]. In a poly-crystalline specimen containing various lattice defects, D_{eff} is written down as

$$D_{eff} = \sum_{i}^{all-states} f_i D_i = f_{H-lat} D_{H-lat} + f_{H-vac} D_{H-vac} + f_{H-GB} D_{H-GB} + f_{H-surf} D_{H-surf} + f_{H-dis} D_{H-dis} + \ldots, \quad (1)$$

$$\sum_{i}^{all-states} f_i = 1, \quad (2)$$

where f_i represents the fraction of H atoms of state-i to all H atoms in the specimen and D_i the diffusivity of H atoms of state-i. For examples, $f_{H\text{-}lat}$ and $D_{H\text{-}lat}$ are respectively the fraction of H atoms located in the lattice, which are tetrahedral interstitial sites in bcc-W, and the diffusivity of the H atoms in the lattice. $f_{H\text{-}vac}$ and $D_{H\text{-}vac}$ are respectively the fraction of H atoms trapped by vacancies and the diffusivity of the H atoms as V-H complexes. $f_{H\text{-}GB}$ and $D_{H\text{-}GB}$ are respectively the fraction of H atoms trapped by GBs and the diffusivity of the H atoms along GBs. Similarly, $f_{H\text{-}surf}$ and $D_{H\text{-}surf}$ are of H atoms located on surfaces, and $f_{H\text{-}dis}$ and $D_{H\text{-}dis}$ are of H atoms trapped by dislocations.

In order for H atoms of a certain state to have a significant contribution to D_{eff}, the product of f_i and D_i needs to be relatively large. For H atoms trapped by vacancies in W, for example, $f_{H\text{-}vac}$ is large due to the strong trap effect of vacancy, while $D_{H\text{-}vac}$ is small as the migration of V-H complexes involves the displacement of vacancy, which requires a large activation energy (1.78 eV [29]). Hence, whether $f_{H\text{-}vac}D_{H\text{-}vac}$ is significant or not is determined by balance between large $f_{H\text{-}vac}$ and small $D_{H\text{-}vac}$. In the case of hydrogen in bcc-Fe, in which V-H interaction is qualitatively similar to that in W [30], it was confirmed by MD simulation that $f_{H\text{-}vac}D_{H\text{-}vac}$ is much smaller than $f_{H\text{-}lat}D_{H\text{-}lat}$ [31]. It should be reasonable to assume that this relation is satisfied also in W based on the similarity on V-H interactions between bcc-Fe and W. Moreover, in thermal desorption experiments of hydrogen in W, rate models were often used to reproduce experimental results with assuming that V-H complexes were immobile [32,33]. This fact also indicates that the contribution of $f_{H\text{-}vac}D_{H\text{-}vac}$ is sufficiently small in W, although there has been no research that quantified $f_{H\text{-}vac}D_{H\text{-}vac}$ in W.

One of the important points regarding the trap effects in the effective diffusivity is that H atoms trapped by GBs, surfaces and dislocations can diffuse along/on them, while H atoms trapped by a deep trap like vacancy hardly diffuse until detrapping. Thus, we cannot neglect the contribution of H atoms trapped at GBs, surfaces and dislocations to the effective diffusivity of hydrogen. Regarding the surface effect, however, since the surface diffusion does not occur perpendicular to the surface, we can neglect it in most experimental settings. Note that the diffusion along GBs or along dislocations are rather isotropic because the networks of GBs and dislocations are almost uniformly spread over the system.

Consequently, if we take into account the five hydrogen states in W, namely H atoms at the lattice sites, at vacancies, at GBs, at surfaces and at dislocations, the effective diffusivity is approximately written as

$$D_{eff} \sim f_{H-lat} D_{H-lat} + f_{H-GB} D_{H-GB} + f_{H-dis} D_{H-dis}, \quad (3)$$

$$f_{H-lat} + f_{H-GB} + f_{H-vac} + f_{H-surf} + f_{H-dis} = 1, \quad (4)$$

Regarding trap effects in hydrogen solubility, the ratio of effective solubility (S_{eff}) to 'true' solubility (S_{true}), which is the solubility in a single-crystal specimen at the equilibrium state where defect concentrations are negligibly low, is expressed as