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# Hydrogen diffusion and vacancy clusterization in iron

# Guocai Lv<sup>a</sup>, Miao Zhang<sup>b</sup>, Hao Zhang<sup>b,c</sup>, Yanjing Su<sup>b,\*</sup>

<sup>a</sup> Basic Experimental Center of Natural Science, University of Science and Technology Beijing, Beijing, 100083, China <sup>b</sup> Corrosion and Protection Center, Key Laboratory of Environmental Fracture (MOE), University of Science and Technology Beijing, Beijing, 100083, China

<sup>c</sup> Department of Chemical and Materials Engineering, University of Alberta, Edmonton, T6G 1H9, Canada

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#### ABSTRACT

Molecular statics and molecular dynamics simulations were performed to study hydrogen diffusion and vacancy clustering in alpha iron. In particular, it was found that hydrogen atom binds very strongly with vacancies, rather than other hydrogen atoms. The mono-vacancies were inclined to form the VH4, VH3, VH2 and VH1 complexes, rather than VH6 in the range of our simulated temperatures. The rate of hydrogen diffusion was apparently reduced in the presence of vacancies, while the vacancy trap effect was gradually weak-ened with increasing temperature. The presence of vacancies changes the diffusion mechanism of H atoms. Moreover, we found that vacancy clusters tended to be formed at the moderate range of temperatures, and fewer clusters were observed at either low or high temperatures. The number of vacancy clusters reduced, while hydrogen-vacancy clusters were gradually created with the increase of hydrogen concentration.

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#### Introduction

Hydrogen (H) can reduce the mechanical properties of materials, especially in Fe-rich materials such as steel [1-3]. Hydrogen-induced cracking is one of the main reasons for the degradation of material properties [4,5]. Many experiments found that the Hydrogen-induced cracking relates to the hydrogen-enhanced voids [6,7]. However, there are still differences in viewpoints about hydrogen's promoting voids in literature. On one hand, it is believed that H has little effect on the nucleation of voids, which only affects the growth and interlinkage of void [8,9]. On the other hand, it is believed that hydrogen enhanced void nucleation [6,10]. For example, Lee and Bernstein [6] found that hydrogen enhanced void nucleation along the characteristic slip bands. Huang et al. [10] found that hydrogen-induced cracking occurred via nanovoid nucleation followed by quasi-cleavage along {111} planes when hydrogen concentration was high. In the case of low hydrogen concentration, hydrogen enhanced ductile fracture via hydrogen-enhanced microvoid nucleation, growth and connection [10]. In situ measurement of high temperature X ray diffraction and thermodynamic calculation showed that hydrogen reduced the vacancy formation energy, so it could increase the local vacancy concentration by several orders of magnitude [11,12]. High vacancy concentration provides a prerequisite for the formation of voids. Subsequently, whether the hydrogen promoted voids can be formed depends on the interaction between H and vacancy. The time scale and volume associated with microscopic processes for interaction

\* Corresponding author.

E-mail address: yjsu@ustb.edu.cn (Y. Su).

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between H and vacancy are out of the range of direct observation by currently available experimental methods, hence, computational methods have become one of the major tools in the investigation and understanding of the microscopic phenomena in H-Vacancy interactions.

The Hydrogen-induced cracking is related to the value of the diffusion coefficient of hydrogen. The diffusion coefficient of H atom in pure Fe was  $10^{-5} \sim 10^{-8}$  cm<sup>2</sup>/s at room temperature measured experimentally [13]. However, the diffusion coefficient of H in theoretical calculation was  $10^{-10}$ – $10^{-9}$  cm<sup>2</sup>/ s [14]. Even in pure Fe, the diffusivity of H atoms was different compared with different crystal structures [15]. In addition, the defects such as vacancies would have great impact on the diffusion of H atoms. For example, Zhu and Oda [16] performed MD simulations calculated the hydrogen effective diffusivities in different bcc-Fe systems, and demonstrated that the diffusivity obviously decreased due to the vacancy trapping effect. The diffusion coefficients of H atoms obtained from experiments and theoretical calculation has a distinct difference. Theoretical calculations rarely take into account the effect of crystal defects on the H diffusion coefficient, which lead to the difference between theoretical calculations and experimental results. Therefore, it is necessary to further study the effect of defects on H diffusion coefficient. It was suggested that once hydrogen atoms diffuse to vacancies, the VH<sub>m</sub> complexes (VHm, where m is the number of hydrogen atoms) could be formed. Experiment [17] showed that VH6 was the most favorable complexes. However, first-principles calculations results showed VH2 complexes were more preferred [18]. Using atomistic simulations, Hayward [19] found low-energy configurations for four, five, and six hydrogen atoms around a monovacancy. It is clear that the trapping of multiple hydrogen atoms at a vacancy in bcc iron is an issue that is still controversial. The combination of vacancy clusters with multiple hydrogen atoms could form vacancy-hydrogen bubbles. Nagumo et al. [20] suggested that the vacancy clusters were internally stabilized by hydrogen atoms and the results led to enhanced plasticity or ductile fracture of materials. Using DFT calculations and molecular dynamics method, Hayward and Fu [21] studied the low energy configuration of hydrogen-vacancy clusters. The results showed that compact or spherical bubbles were more energetically favorable than planar or linear configurations. Although the vacancy-hydrogen bubbles in bcc-Fe have been studied, the mechanism of the interaction between vacancy clusters and H atoms is still not clear. In particular, there is no report on the interaction mechanism between vacancy clusters and hydrogen at different temperatures. In contrast to the previous reports [13-28], the overall influence of vacancy on the diffusivity of hydrogen, the most stable configuration of VHm, the mechanism of the interaction between vacancy clusters and H atoms, are not systematically studied.

In the current paper, we approach these topics from several angles, paying close attention to the dynamic interaction between H and vacancy. We examine the atomistic behavior of hydrogen and vacancy in bcc-Fe using Molecular Statics (MS) and MD methods. The vacancy trapping effect was investigated by studying the binding energy between hydrogen and vacancy and by examining the self-part of the van Hove function of H atoms. The configurations of hydrogen with monovacancy were analyzed and the diffusion coefficient of hydrogen with different vacancy concentrations was calculated. In addition, MD method was employed to study the size of vacancy clusters with and without hydrogen. The result show that vacancy binds strongly with hydrogen that it makes impact on the diffusion rate of H atom, meanwhile, the configuration of vacancy clusters is reduced with hydrogen concentration.

#### **Computational methods**

Atomistic simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [29,30]. An embedded atom method (EAM) potential is used to describe the interactions between iron and hydrogen, which was developed by Ramasubramaniam et al. [18], and then modified by Jun Song and W. A. Curtin [31]. For this potential (Potential A in Ref. [31]), Fe–Fe interactions were taken from Mendelev et al. [32], while the Fe–H and modified H–H interactions were fit from density functional theory (DFT) calculations [18,31]. The modified potential introduces an additional repulsive term into the pairwise potential for H–H interaction, thus it avoids spontaneous clustering of bulk H in the matrix, and makes the interaction between H–H consistent with the phase diagram for Fe–H.

In this study, periodic boundary conditions were applied along three axes and a box of size  $20a_0\times 20a_0\times 20a_0$  along the [100], [010] and [001] directions was used, where  $a_0$  is the lattice parameter of bcc-Fe at the temperature of interest. It is suggested that the simulation box size effect is negligible as far as the box size is large enough [22]. In majority of previous computational studies in bcc-Fe, it was suggested that the tetrahedral sites (T sites) were the most energetically favorable positions of a single hydrogen atom [24,33]. Here the hydrogen atoms were first added randomly at T sites in bcc-Fe, and vacancies were created by taking away Fe atoms randomly. Based on the modified potential [31], the binding energies of H-H, H with vacancy, and vacancy with vacancy in bcc-Fe were studied through MS simulations using the defect binding energy equation. The binding energy of *n* defects  $\{A_i\}$ can be written as [34]:

$$E_b(\{A_i\}) = \sum_{i=1}^n E(A_i) - [E(\{A_i\}) + (n-1)E_0]$$
<sup>(1)</sup>

where  $E(A_i)$  is the energy of the configuration containing only  $A_i$ ,  $A_i$  represents ith perfect,  $E(\{A_i\})$  is the energy of the configuration with all *n* defects, and  $E_0$  refers to a configuration containing no defects or impurities (i.e., bulk bcc Fe). Following this definition, a positive value of binding energy implies an attractive interaction and vice versa.

MD simulation was used to calculate the hydrogen diffusivity and examine the vacancy clustering in bcc-Fe at different vacancy concentrations. In our study, 160 hydrogen atoms were initially introduced randomly in T sites. The size of the simulation box is  $20a_0 \times 20a_0 \times 20a_0$  containing 16000 bcc lattice sites with the initial H concentration of 1 at. % Vacancies were randomly distributed to reach the concentrations of 0.1, 0.2, and 0.3 at. % in the simulation box.

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