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Hydrogen solubility in hcp titanium with the account of vacancy complexes and hydrides: A DFT study

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ABSTRACT

The saturation solubility of hydrogen with respect to titanium hydrides, and the concentration of H-vacancy complexes in α-Ti are predicted on the basis of a thermodynamic model and *ab initio* calculated free energies. The presence of hydrogen increases the vacancy complex concentration by several orders of magnitude, with most of these complexes containing three H atoms. We show also that the solubility of hydrogen within the titanium is strongly influenced by the temperature-dependent free energy terms, and that by including these terms in the thermodynamic model it is possible to obtain good agreement with experiment.

1. Introduction

For titanium alloys, hydrogen has significant importance from negative as well as positive points of view. On the one hand, the formation of hydrides causes embrittlement of all types of alloys such as $\alpha, \alpha+\beta$ and β alloys [1]. On the other hand, hydrogen is extensively used as a temporary alloying element providing the additional type of Ti alloys treatment known as thermohydrogen processing [2]. This treatment has several advantages; it increases tensile strength and ductility, improves sinterability of powder compacts, and leads to the grain refinement. Owing to the after-treatment removal of hydrogen, the further embrittlement is excluded.

Although, for binary Ti-H system, the influence of hydrogen has been extensively studied experimentally [3–10], still a lot of additional investigations are needed for more complex systems, which include the Ti alloys commonly used in industry (such as Ti–6Al–4V) and novel nanocrystalline Ti materials [11]. To improve the rate and quality of investigations, the experimental study should be complemented by computer simulation approaches, which provide unprecedented results on the atomic level and allow predicting multicomponent phase diagrams. However, there are many challenges on the way to a simulated phase diagram, which does not include experimental data. One of the examples of such challenges is the solubility limit of hydrogen. It was found that for beta alloys, such as Ti–Mo–Nb–Al [12] and Ti–V–Fe–Al [13], the embrittlement, due to hydrides formation, takes place at a concentration far below the solubility limit of 50 at.% in pure β-Ti. This shows that alloying elements could significantly influence the solubility of hydrogen, and its theoretical prediction would be useful.

However, the comparison of known experimental and theoretically calculated phase diagrams shows that the theory has failed to predict the solubility of hydrogen, even in pure α-Ti. For example, the experimental value of solubility at 600 K is of the order of 6.7 at.% [7], but in the work of Xu et al., based on first-principles and cluster expansion method, it is significantly underestimated ($\sim$1 at.%) [14]. Several factors could be responsible for this disagreement, but the most probable one is the omission of vibrational entropy and its influence on the hydrogen solution energy [14]. There are a number of studies, in which the Ti-H phase diagrams are assessed using thermodynamic approaches [15–18], however, in predicting the solubility, experimental data were used.

Coming back to the application of hydrogen as a temporary alloying element, we should mention that several positive effects caused by hydrogen, such as refinement of the structure after welding, improvement of powder alloys sintering, formation of a nanocrystalline structure, among others, are closely associated to the influence of hydrogen on diffusion processes [2]. Since the mechanisms of diffusion are determined by the vacancies in the material, the study of hydrogen-vacancy interaction is, therefore, very important. Indeed, the interaction of hydrogen with vacancies was extensively studied from first-principles [19], including the calculation of H diffusion coefficients [20,21]. However, despite

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the experimental indications, the influence of hydrogen on the vacancy concentration was never evaluated [22].

Keeping in mind the problems outlined above, the aim of our work is to estimate the impact of vibrational entropy on the solubility of hydrogen, and to predict H influence on the vacancy concentration in α-Ti. In order to calculate the free energies of constituents at zero and finite temperatures, we use first-principles density functional theory in combination with harmonic approximation. In assessing the Ti-H hydrides, we extensively study the influence of c/a ratio on their formation energies and stability. Finally, the investigation of hydrogen influence on vacancy concentration is carried out with the help of a recently developed model for superabundant vacancy (SAV) description [23].

2. Computational details

To optimize the geometry of considered Ti-H structures and calculate their total energies we used ABINIT [24] and VASP [25] *ab initio* packages. Both packages implement density functional theory (DFT) [26,27] using plane-wave basis set and support projected augmented wave (PAW) formalism [28].

To describe $3s, 3p, 4s, 3d$ valence electrons of titanium (12 electrons in total) and $1s$ electron of hydrogen we have used PAW potentials constructed within the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) form [29]. To ensure the convergence of results the following calculation parameters were chosen. The kinetic energy cutoff was set to 700 and 441 eV for ABINIT and VASP calculations, respectively. The spacing between k-points in the Brillouin-zone was $\sim$0.15 Å^{-1}. The smearing of the Fermi surface was obtained with the Methfessel-Paxton method [30] and a smearing width of 0.14 eV and 0.2 eV was used in ABINIT and VASP calculations. Finally, the full structural relaxations were performed until the forces acting on atoms were less than 2.5 meV/Å in ABINIT calculations and 5 meV/Å in VASP calculations.

To insure that VASP and ABINIT packages provide consistent results, a number of calculations were performed twice. It was found that the results obtained with different packages are very close to each other. From the results obtained with ABINIT, we present the formation energies of 27 titanium hydrides depending on c/a ratio, thermal properties for three hydrides, and the formation energies of H-vacancy complexes. All other presented results, including thermal properties and formation energy of δ-TiH$_2$ relative to H solid solution, were obtained with VASP code.

To calculate cohesive energy of H$_2$ molecule in vacuum we have used $10 \times 10 \times 10$ Å supercell, which ensured convergence in total energy of 0.1 meV per one H atom. The titanium hydrides with different stoichiometry were constructed using face centered cubic (fcc) Ti supercell with four titanium atoms (cubic supercell). To model the hydrogen solid solution the $3 \times 3 \times 3$ (Ti$_{54}$H) hcp-Ti supercell was found to be enough to reproduce the solution energy with 8 meV precision.

To find stable positions of the H atoms inside the titanium vacancy three stages of relaxation were applied in the following order: (i) molecular dynamics simulation at 300 K with the velocity Verlet algorithm [31]; (ii) cooling down to 100 K using Nose–Hoover thermostat [32]; (iii) relaxation of the obtained supercells using Broyden-Fletcher-Goldfarb-Schano method [33] at 0 K.

To account the contribution of lattice vibrations in the free energies, we calculated them using harmonic approximation. The phonon densities of states (PHDOS) were calculated on the $36 \times 36 \times 36$ q-point grid through the diagonalization of the dynamical matrix at each q-point as implemented in the PHONOPY code [34].

The force constants required for construction of the dynamical matrix were computed using direct supercell approach. In this approach, the non-equivalent atoms are displaced in most symmetrical directions after which the resulting Hellmann–Feynman forces acting on atoms are calculated. The displacement step was 0.03 Å. For hydrides and hcp solid solution the force constants were calculated in $2 \times 2 \times 2$ cubic fcc-Ti supercell with 32 Ti atoms and $3 \times 3 \times 3$ hcp-Ti supercell with 54 Ti atoms, respectively.

3. Structure and energy of constituents in Ti-H system at 0 K

To determine the solubility of hydrogen, one has to first consider the constituents involved in the system and determine their free energies. In the current work, in order to reduce the complexity of the considered system, we omit the titanium bcc phase (β-Ti) from the evaluation. For this reason, our model Ti-H system includes gaseous H$_2$, hydrogen solid solution in hcp titanium (α-Ti), several titanium hydrides (TiH$_x$), and H-vacancy complexes. Since we completely rely on first-principles data, and do not use empirical fitting to the experiment (except the free energy of H$_2$ gas taken from NIST-JANAF tables [35]), it is natural to first describe all constituents at zero Kelvin temperature.

3.1. The description of gaseous H$_2$ phase and H solid solution in α-Ti

The free energy of H$_2$ gas is shifted by a certain value depending on the chosen PAW potentials. At zero pressure and zero temperature, we define the chemical potential of hydrogen as half of the energy of a H$_2$ molecule in vacuum, which is –3.383 eV for H potential used in VASP. The calculated values of the cohesive energy E_c and bond length of H$_2$ molecule are 4.544 eV and 0.751 Å, respectively. They are in good agreement with experimental values of 4.748 eV and 0.742 Å [10], and theoretical values of 4.532 eV and 0.746 Å obtained by Tao et al. using the PAW GGA approach [36].

For pure α-Ti, we obtained the lattice parameters $a = 2.937$ Å and $c = 4.646$ Å, which are in good agreement with experimental as well as previously calculated results [37,38]. To model the hydrogen solid solution, we put H into octahedral and tetrahedral interstitial voids of α-Ti. According to the recent studies, the H solution energies in these types of voids are very close (–0.62 eV and –0.56 eV at 0 K [20]), meaning that accounting of both interstitial types is needed for correct predictions of H solubility.

It is assumed that the approximation of dilute solid solution could be applied to the hydrogen in α-Ti [14]. This could be appropriate for the concentrations lower than 1 at.%, however it is known that the maximum solubility of H in α-Ti reaches $\sim$6.7 at.% and for such concentration the distances between H atoms are of the order of 6 Å, at which noticeable interactions could exist. To check this, we considered several hcp-Ti supercells which model different concentration regimes: Ti$_2$H ($1 \times 1 \times 1$), Ti$_8$H ($2 \times 2 \times 1$), Ti$_{16}$H ($2 \times 2 \times 2$), Ti$_{54}$H ($3 \times 3 \times 3$), and Ti$_{96}$H ($4 \times 4 \times 3$).

The solution energies and volumes of hydrogen in α-Ti per one H atom at 0 K were calculated as follows:

$$\begin{aligned} \Delta E_{sol} &= E(\mathrm{Ti}_m\mathrm{H}) - E(\mathrm{Ti}_m) - \frac{1}{2}E(\mathrm{H}_2), \\ \Delta V_{sol} &= V(\mathrm{Ti}_m\mathrm{H}) - V(\mathrm{Ti}_m), \end{aligned} \qquad (1)$$

where $E(\mathrm{Ti}_m\mathrm{H})$ and $V(\mathrm{Ti}_m\mathrm{H})$ are the total energy and volume of supercell containing m Ti atoms and one H atom in octahedral or tetrahedral void, $E(\mathrm{Ti}_m)$ and $V(\mathrm{Ti}_m)$ are the total energy and volume of corresponding supercell with pure α-Ti, and $E(\mathrm{H}_2)$ is the total energy of hydrogen molecule in vacuum. The values of solution