Materials Chemistry and Physics 148 (2014) 533–539

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Energy and diffusion of hydrogen atoms in titanium substituted vanadium hydrides from ab initio calculations

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HIGHLIGHTS

- Ti substitution expands any crystal structure of vanadium metal or hydride.
- H atoms are repulsed by Ti atoms despite their high electrochemical affinity.
- Strong electrochemical bonding between Ti and H lowers the formation energy.
- Ti substitution reduces hydrogen diffusion by over 90% at room temperature.

ARTICLE INFO

Article history:
Received 6 August 2013
Received in revised form
9 June 2014
Accepted 23 July 2014
Available online 20 September 2014

Keywords:
Computational technique
Thermodynamic properties
Diffusion
Electronic structure

ABSTRACT

The equilibrium lattice parameters, formation energy, and diffusion behavior of hydrogen atoms in vanadium hydrides with and without Ti substitution were calculated by ab initio calculations and quantum correction by zero point energy was achieved using phonon vibration calculations. The calculated formation energies indicated that Ti substitution induces instability in the vanadium hydrides and electron density calculations showed that hydrogen has strong electrochemical affinity with Ti. The diffusion behavior was examined by the nudged elastic band (NEB) method to investigate the transition states of the hydrides. It revealed that Ti substitution is shown to reduce the diffusion coefficient and this effect was decreased with increasing temperature. The results of this study are expected to provide useful guidelines for understanding hydrogen absorption and desorption properties of hydrogen storage materials.

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1. Introduction

Hydrogen storage is an important field of research because of hydrogen's abundance, highly efficient energy release, and lack of polluting exhaust products [1]. However, its use as an effective fuel is hindered by problems with its storage and its low energy density. Previous studies have sought to overcome these obstacles and develop materials that allow the efficient storage and use of hydrogen [2,3], with metal hydrides being the most effective storage materials so far developed.

The high capacities for hydrogen storage shown by vanadium metal and vanadium-based alloys make them promising storage materials [4–7]. These materials have a stable BCC crystal structure (α) at room temperature and pressure. They absorb hydrogen in an activated condition and readily form β (BCT) phase hydrides, such as V_2H or VH [8]. Further absorption forces phase transformation from β to γ (FCC) phase hydrides (VH or VH_2). Eqs. (1)–(3) represent the hydrogen absorption reaction system.

$$2V\ (\alpha) + 1/2H_2 \leftrightarrow V_2H\ (\beta) \tag{1}$$

$$V_2H\ (\beta) + 1/2H_2 \leftrightarrow 2VH\ (\beta + \gamma) \tag{2}$$

$$2VH\ (\beta + \gamma) + H_2 \leftrightarrow 2VH_2\ (\gamma) \tag{3}$$

The β phase is stable, so hydrogen does not desorb under moderate conditions. However, the γ phase is unstable and desorption is possible at certain temperatures and pressures [9]. Consequently, only half of the initially introduced hydrogen can be released, thereby restricting the material's practical applicability. Therefore, control of the metal hydride's stability is essential to increasing the amount of hydrogen available as fuel.

The alloying of secondary elements has been used to control the stability and other properties of metal hydrides. Maeland et al. [10] experimentally investigated the hydride formation rates of solid solutions of vanadium and various secondary metals such as Co, Fe, and

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http://dx.doi.org/10.1016/j.matchemphys.2014.07.033
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Ni. They found that the strain induced by alloying reduced the surface trapping energy, thus allowing rapid hydrogen absorption. Yukawa et al. [11] reported that small amounts of various secondary and ternary 3d-, 4d-, and 5d-transition metals affected the stability of vanadium hydrides with β-phase (VH or V_2H), and Nakamura et al. [12] synthesized a ternary Ti–V–Mn alloy with BCC structure and used neutron and X-ray powder diffraction to obtain the accurate crystal structures of two metal hydrides formed from the alloy. Cho et al. [13,14] also investigated the crystal structure, hydride formation energy, and equilibrium hydrogen pressure change of ternary Ti–Cr–V alloys. Despite previous efforts [9–15], a detailed and quantitative understanding of the effects of alloying is yet to be established, and this limits our ability to improve the hydrogen storage capacity of metal hydrides.

Therefore, this work investigates, via ab initio calculations, the quantitative effects of Ti substitution on the geometry and formation energy of vanadium metal and vanadium hydrides, as well as the effects of alloying on the diffusion behavior of hydrogen within the alloy structures. The accuracy of our calculated results is tested through comparison with available experimental results of vanadium metals and hydrides. Zero point energy (ZPE) corrections are considered for each vanadium metal and hydride structure to allow a direct comparison with the experimental results.

2. Calculation methods

Spin polarized ab initio calculations were performed using the Vienna Ab initio Simulation Package (VASP), which implements DFT using a plane wave basis set [16–18]. Exchange–correlation effects were treated in the framework of the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA) and the Perdew–Wang local density approximation (LDA) [19,20]. Integration in the Brillouin zone was conducted using 13 × 13 × 13 Monkhorst Pack k-points for the vanadium metal and hydride structures, and 13 × 13 × 7 k-points for the HCP titanium metal structure. We employed a high-energy cutoff of 600 eV with an energy convergence of 0.01 eV atom^{-1}. The Methfessel–Paxton technique with a smearing width of 0.1 eV was used for the energy calculations [21]. The energy of a hydrogen molecule was computed using the same potential in a 10 × 10 × 10 Å^3 box. The electronic total energy in all the calculations was converged to 10^{-6} eV cell^{-1} and the structure relaxation was conducted to obtain the equilibrium crystal information and the total electronic energy of each model. To assess quantitatively the effects of Ti concentration, we employed supercell approaches: 2 × 2 × 2 and 3 × 3 × 3 for α phase vanadium metals; 2 × 2 × 2 for γ phase vanadium hydrides and 2 × 1 × 1 for β phase vanadium hydrides. Phonon spectra for the solids and vibrational frequencies of the molecular H_2 were calculated to obtain the ZPE in each case using the small displacement method, as implemented in the VASP code [22,23]. Depending on the model, between 2 and 60 supercells with displacements of ±0.03 Å of the non-equivalent atoms were used to calculate the phonon vibrational properties of the solids.

The nudged elastic band (NEB) method was used to determine diffusion pathways and diffusion energy barriers [24,25]. Model images of the intermediate steps were generated automatically during computation, and each image was relaxed until the maximum residual force reached below 0.01 eV Å^{-1}. After relaxation, ZPE calculations were performed on each model with displacements of ±0.03 Å.

3. Results and discussion

3.1. Geometry

The reliability of the calculations was assessed via comparison with experimental results using well-known vanadium-based structures; the calculated results agree well with the experimental results (Table 1). Both GGA and LDA calculations underestimate the lattice parameters, but differences from the experimental data are below 5%. GGA calculations are more accurate than LDA calculations under the considered conditions, as calculations using LDA exchange–correlation potentials generally overestimate the binding energy and so give greater underestimates of the lattice parameters [28–30]. The models increase in volume with increasing hydrogen content, in good agreement with the general trend of hydrogen absorption.

Table 2 lists the geometries of vanadium metals and hydrides with different levels of Ti substitution. Ti substitution induces volume expansion in all the crystal structures. Nearly all the lattice parameters increase with increasing Ti concentration (C_{Ti}). The exception is the contraction of the *x*-axis parameter of the β-phase vanadium hydrides, which is overcompensated by lattice expansion on the *z*-axis. As a result, the volume of the β-phase vanadium hydrides increases with increasing C_{Ti}. The volume of vanadium metals and hydrides greatly influences their hydrogen storage properties, such as plateau pressure (P^{eq}) [31]. The volume expansion due to Ti substitution increases the size of interstitial holes for the introduction of hydrogen; therefore, P^{eq} can be expected to decrease with increasing C_{Ti} in the vanadium-based metals and hydrides.

Though the GGA and LDA calculations yielded the reasonable structural information compared with the experimental results, the GGA calculations are more accurate, as mentioned above. Therefore, we adopted the calculation results from the GGA in the other sections of present investigation.

3.2. Formation energy

The preferred interstitial site for hydrogen atoms in the vanadium hydrides is the tetrahedral site (T-site). This was elucidated by calculating the hydride formation energies for V_2H_1 and $V_2H_{0.125}$ at absolute zero temperature (0 K). The hydride formation energy ($\Delta E_0^{hydride}$) is expressed as follows:

$$\Delta E_0^{V_2H_1,bcc} = \left[\mathrm{E}_{el}\left(V_2H_1^{bcc}\right) - E_{el}\left(V_2^{bcc}\right) - \frac{1}{2}\mathrm{E}_{el}(H_2)\right] + \left[\mathrm{E}_{ZPE}\left(V_2H_1^{bcc}\right) - \mathrm{E}_{ZPE}\left(V_2^{bcc}\right) - \frac{1}{2}\mathrm{E}_{ZPE}(H_2)\right] \quad (4)$$

$$\Delta E_0^{V_2H_{0.125},bcc} = \left[\mathrm{E}_{el}\left(V_2H_{0.125}^{bcc}\right) - E_{el}\left(V_2^{bcc}\right) - \frac{1}{16}\mathrm{E}_{el}(H_2)\right] + \left[\mathrm{E}_{ZPE}\left(V_2H_{0.125}^{bcc}\right) - \mathrm{E}_{ZPE}\left(V_2^{bcc}\right) - \frac{1}{16}\mathrm{E}_{ZPE}(H_2)\right] \quad (5)$$

Table 1
Geometric information of vanadium metals and their hydrides calculated by ab initio calculations.

Model	a_{cal}^{G} (Å)	a_{cal}^{L} (Å)	a_{exp} (Å)	Vol.^{G} (Å^3)	Vol.^{L} (Å^3)	Δa^G (%)	Δa^L (%)
V_2 (α)	2.998	2.930	3.03[a]	26.96	25.15	−1.06	−3.30
V_4 (γ)	3.818	3.733		55.67	52.00		
$(V_2H)_8$ (β)	a: 2.945	a: 2.885	a: 3.03[a]	28.98	27.24	a: −2.81	a: −4.79
	c: 3.341	c: 3.273	c: 3.38[a]			c: −1.15	c: −3.17
			a: 3.02[b]			a: −2.48	a: −4.47
			c: 3.33[b]			c: 0.33	c: −1.71
$(VH_2)_4$ (γ)	4.215	4.140	4.270[c]	74.89	70.96	−1.29	−3.05

$\Delta a^G = (a_{cal}^G - a_{exp})/a_{exp}$.
$\Delta a^L = (a_{cal}^L - a_{exp})/a_{exp}$.
G and L indicate GGA and LDA exchange correlation functional, respectively.
[a] Ref. [8].
[b] Ref. [26].
[c] Ref. [27].

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