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The influence of pre-adsorbed Pt on hydrogen adsorption on B2 FeTi(111)

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ABSTRACT

The hydrogen adsorption properties on a Pt covered Fe-terminated B2-FeTi (111) surface are studied using the Density Functional Theory (DFT). The calculations are employed to trace relevant orbital interactions and to discuss the geometric and electronic consequences of incorporating one Pt atom or a Pt monolayer on top of the FeTi surface. The most stable adsorption site is a distorted FCC hollow for one Pt atom and from this location we build the Pt monolayer (ML). The H-adsorption energy is very close among BRIDGE, HCP and FCC hollow sites (~ -0.45 eV) being lower for the TOP site (-0.34 eV) in the case of a Pt(111) fcc surface. In the case of a Pt ML/FeTi, the H more stabilized on a BRIDGE site (~ -1.13 eV) interacting with both a Pt and Fe atom. We also computed the density of states (DOS) and the overlap population density of states (OPDOS) in order to study the evolution of the chemical bonding after adsorption.

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1. Introduction

Hydrogen as an energy carrier is expected to play a crucial role in a future more sustainable society due to the decline of the world's crude oil production. However, one of the key challenges for developing a new clean energy system using hydrogen is associated with its reversible storage, transportation and production [1]. Although several materials have been developed for hydrogen storage [2,3], such as metal-organic frameworks (MOFs) [4–7], covalent-organic frameworks (COFs) [8], carbon nanomaterials [9,10], zeolites and mesoporous materials [11], none of them meet the ideal requirements specified by the US Department of Energy (DOE) for H-storage materials. According to the DOE, a 9.0 wt%

gravimetric density and 81 g/L volumetric density is the threshold for a sustainable hydrogen storage system [12].

Taking into account both safety and cost, metal/alloy hydrides are good candidates for hydrogen storage [13]. Ivey & Northwood [14] and Sakintuna et al. [15] reviewed many intermetallic alloys that have been studied so far.

Recently, Hout et al. [16] reviewed the recent progress within the experimental methods for preparation of hydrogen storage materials. These authors focus on mechanochemical synthesis method for solid hydrogen storage. The synthesis of innovative materials for energy conversion and storage has received increasing focus during the past decades due to the world's increasing energy demands and simultaneous needs for environmentally friendly energy technologies [16].

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Among AB-type intermetallics, FeTi compound is one the most promising hydrogen storage alloys due to its low cost, reversible character for hydriding/dehydriding at near ambient conditions, store capacity of 1.9 wt% hydrogen and kinetics of hydrogen absorption/desorption [17–21]. On the other hand, Reilly & Wishwall [22] observed that this alloy reacts with hydrogen to form two ternary hydrides, i.e., FeTiH_{~1} and FeTiH_{~2} [23,24]. However, the two main drawbacks of this material are: i) the activation process that it requires high heating temperatures ~400 °C and a considerable hydrogen pressure and ii) sensitivity to impurities in the hydrogen gas. This leads to formation of an oxide layer preventing the hydrogen adsorption [18,22,25–30].

As well known, the FeTi hydrogen storage alloy exhibits sluggish rates of H₂ absorption because of stable surface oxide layers. The occurrence of H₂ dissociation is caused by the exchange of electrons between the H₂ molecules and the metal surface [31,32]. Oxide layers on the metal surface hinder the electron exchange and the subsequent H₂ dissociation. This process retards the whole reaction rate of hydrogen adsorption. A nano-structured FeTi alloy (n-FeTi) exhibits remarkably high rates of initial activation and hydrogen absorption compared with those of an untreated FeTi alloy [21]. Edalati et al. [33] shows that FeTi processed by high-pressure torsion (HPT) absorbs and desorbs 1.7 wt% hydrogen at room temperature without activation. The absorption pressure decreases from 2 MPa in the first hydrogenation cycle to 0.7 MPa in the latter cycles.

Several experimental [18,25,34–37] and theoretical [38–42] studies in FeTi showed that the formation of an oxide layer can be prevented by the usage of noble metal coating, such as palladium and platinum.

Bououdina et al. [43] and Heller et al. [44] considered Ni, which is not as expensive as Pd, as coating material. However, the Ni surface is sensitive to CO from air [44]. Moreover, platinum is a well-known electrocatalytic material and is primarily used for fuel-cell applications [2,45–48].

Hydrogen sorption performances of FeTi are very sensitive to the preparation conditions, especially ones that result in contamination of the material with oxygen. The effect of oxygen introduction into FeTi alloy was investigated by Davids et al. [49]. These authors observed that the increase of oxygen content in the alloy results in the decrease of the abundance of the main FeTi phase, together with the increase in the abundance of Ti₄Fe₂O_{1-x}. This effect is well-pronounced even at low (0.1–0.2 wt%) oxygen concentrations, as well as when titanium is taken in excess as compared to the stoichiometric Ti:Fe ratio. The introduction of oxygen improved activation performances of the FeTi based material, but decreased its reversible hydrogen absorption capacity.

Solid-oxide-oxygen-ion conducting membrane (SOM) process is a novel, high efficient, low cost, energy-saving, environmentally friendly electrochemical extraction method of metals or alloys. Taking FeTi based hydrogen storage alloy as an example, the authors demonstrated the possibility of SOM process to produce hydrogen storage alloy directly from the oxide; the electrochemical performances of the obtained alloy are also investigated [50].

In this work, a Fe-terminated B2-FeTi (111) slab is considered to study the adsorption of H with a Pt-monolayer (ML).

We used the concepts of density of state (DOS) to trace the relevant electronic interaction and overlap population density of states (OPDOS) to characterize the changes in the chemical bonding after hydrogen adsorption.

2. The surface model and the computational method

The inter-metallic B2-FeTi structure is bcc with a lattice parameter $a_0 = 2.976 \text{ \AA}$ [51,52]. The unit cell for this structure is shown in Marchetti et al. [41].

The (111) crystallographic plane was selected to perform our study to compare with previous work from Kulkova et al. [39]. The theoretical method and the surface model are considered in the next sections.

2.1. Computational method

We performed first-principles calculations based on spin polarized DFT. The Vienna *Ab-initio* Simulation Package (VASP) is used to solve Kohn–Sham equations with periodic boundary conditions and a plane wave basis set [53–55]. Electron-ion interactions are described by ultra-soft pseudo-potentials [56], exchange and correlation energies are also calculated using the Revised Perdew–Burke–Ernzerhof form of the spin-polarized generalized gradient approximation (GGA-RPBE), which has been shown to give accurate values for adsorption energies of many molecular species [57]. We used a kinetic energy cutoff of 300 eV for all calculations, which converges total energy to ~1 meV/atom and 0.001 Å for the primitive bulk cell. The Monkhorst–Pack scheme is used for k-point sampling [58]. An equilibrium lattice constant of $a_0 = 2.946 \text{ \AA}$ is used and it was obtained with a $7 \times 7 \times 7$ converged mesh within the first Brillouin Zone. The geometry optimization was terminated when the Hellman–Feynman force on each atom was less than 0.02 eV/Å and the energy difference was lower than 10^{-4} eV. The lattice constant is in agreement with experimental XRD data. Bader analysis is used to calculate electronic charges on atoms before and after H adsorption [59].

In the case of one Pt atom in each adsorption site and a Pt ML, the Pt adsorption energy is calculated by:

$$\Delta E_{ads} = [E_{Total}(FeTi_{slab} + nPt) - nE_{Total}(Pt) - E_{Total}(FeTi_{slab})]/n \quad (1)$$

where n is the number of Pt atom considered; $E_{Total}(FeTi_{slab} + nPt)$ is the total energy of the relaxed Pt/FeTi system; $E_{Total}(Pt)$ is the total energy of an isolated Pt atom and $E_{Total}(FeTi_{slab})$ is the total energy of the relaxed clean FeTi(111) slab.

After H adsorption, the stabilization of Pt ML/FeTi + H can be better investigated by comparing the adsorption energies of Pt ML/FeTi – starting from the intermetallic surface and molecular hydrogen – given by:

$$\Delta E_{ads} = E_{Total}(H/Pt ML/FeTi) - E_{Total}(Pt ML/FeTi) - \frac{1}{2}E_{Total}(H_2 \text{ molecule}) \quad (2)$$

where $E_{Total}(H/Pt ML/FeTi)$ is the total energy of the relaxed FeTi(111) covered by a Pt ML after H adsorption, system, E_{Total}

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