Journal of Alloys and Compounds 696 (2017) 548–559

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Ab-initio study of hydrogen mobility in the vicinity of MgH_2–Mg interface: The role of Ti and TiO_2

Radojka Vujasin [a], Jasmina Grbović Novaković [a], Nikola Novaković [a, *], Simone Giusepponi [b], Massimo Celino [b]

[a] Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001, Belgrade, Serbia
[b] ENEA, C. R. Casaccia, Via Anguillarese 301, 00123 Roma, Italy

ARTICLE INFO

Article history:
Received 18 July 2016
Received in revised form
12 November 2016
Accepted 19 November 2016
Available online 22 November 2016

Keywords:
Ab–initio calculations
Hydrogen storage
Hydrogen desorption
Interfaces
Dopants
Oxidation

ABSTRACT

Doping of MgH_2 with transition metals and their oxides is well-known procedure to improve its hydrogen (de)sorption properties, namely to lower the temperature of desorption and to achieve the kinetics speedup. In order to assess the influence Ti and TiO_2 doping has on H mobility and to characterize structurally and electronically observed differences, MgH_2–Mg interface doped with both Ti and TiO_2 have been studied using ab-initio interface molecular dynamics and bulk calculations. Results suggest different mechanisms of MgH_2 structure destabilization. The presence of dopants significantly stabilize MgH_2–Mg interface, which is confirmed by work of adhesion computation. Calculated formation energies show that interface system with doped TiO_2 is more stable. In terms of H mobility, molecular dynamics simulations confirm that Ti doping is more effective than TiO_2 in lowering the desorption temperature. The mobility of hydrogen atoms close to dopant is much higher in the case of Ti than in the case of TiO_2. Electronic structure characterization reveals that oxygen atoms with high electron affinity forms more pronounced ionic bonding with Ti and the other neighbor Mg atoms. This in turn cause a shorter Ti–H bonds in first coordination than in the case of Ti doping and further reduction of H atoms mobility. This is in accordance with molecular dynamics predictions.

1. Introduction

Among the Mg–based alloys which are found to be promising materials for hydrogen storage, MgH_2 is distinguished for its high gravimetric energy density (7.6 wt%), low cost and non-toxicity [1]. There are drawbacks, like high hydrogen desorption temperature (447 °C for pure MgH_2) and sluggish desorption kinetics, that still prevents the use of MgH_2 in practical applications. Many different approaches, supported by numerous experimental and theoretical investigations have been proposed to overcome the aforementioned drawbacks. For example, both nanostructuring of MgH_2 by mechanical milling and the addition of transition metals (TM), their oxides and intermetallics, were found to decrease desorption temperature and improve (de)hydriding kinetics [2–5].

A general mechanism of (de)hydriding reaction can be described using following steps [6,7]: (a) hydrogen in the bulk gas phase transfers to the surface of the metal particle; (b) hydrogen diffusion through the boundary layer between a gas phase and a solid particle; (c) physisorption of hydrogen molecules on the solid surface; (d) dissociation of hydrogen molecules and chemisorption; (f) surface penetration of hydrogen atoms; (g) diffusion of hydrogen atoms through the hydride product layer to the hydride/metal interface. Any of these steps can be rate limiting and determine the kinetics. Addressing the diffusion of hydrogen atoms through the hydride layer to the hydride/metal interface is of great importance in improving the sorption process.

The addition of titanium, an early 3d TM in the role of MgH_2 (de) sorption catalyst, was the subject of both experimental and theoretical types of research. As suggested by Dai et al. [8] Ti atoms can occupy both substitutional and interstitial sites in the MgH_2 lattice. Ti also tends to change its local environment and to form the local structural arrangement similar to the one found in fluorite type TiH_2. On the other hand, Chen et al. [9] in their theoretical work concerning TM doping in MgH_2 have concluded that doping effects (like variations of ionicity) are localized strictly around TM

* Corresponding author.
E-mail addresses: radojka.vujasin@vinca.rs (R. Vujasin), jasnag@vinca.rs (J. Grbović Novaković), novnik@vinca.rs (N. Novaković), simone.giusepponi@enea.it (S. Giusepponi), massimo.celino@enea.it (M. Celino).

http://dx.doi.org/10.1016/j.jallcom.2016.11.250
0925-8388/

impurities and are almost TM atom independent. Paskaš Mamula et al. [10] have also found that the influence of TM doping is localized within several nearest coordination shells. They have found that ionicities of both TM and nearest neighbor H atoms follow the trend in bonding lengths throughout the TM series. TM–H bonds were found to be the shortest for late 3d metals and only slightly shorter than Mg–H in Ti case. Moreover, Ti doping can lower the stability of MgH_2 and increase the enthalpy of formation. This result was confirmed in another theoretical study by Song et al. [11]. They also emphasized the importance of TiH_2 formation and its negative impact on overall performance of Ti-doped MgH_2. This is one of the reasons to use oxides, specifically TiO_2, as dopants.

A large number of experimental studies confirm that the addition of metal oxides, such as TiO_2, Al_2O_3, V_2O_5, Nb_2O_5 and Fe_3O_4, has beneficial effect on destabilization of MgH_2 matrix and cause improvement of kinetic properties of this material [5,12–15]. Barkhordarian et al. [16] suggested that the catalytic activity of transition metal oxides are influenced by four distinct physicochemical properties: high number of structural defects, low stability of the compound, high valence state of the transition-metal ion within the compound and high affinity of the transition-metal ion for hydrogen. Among the various metal oxides used as catalysts, TiO_2 is noteworthy because it has low cost and high availability, besides its great catalytic characteristics [17]. As shown by Jung et al. [14] addition of only 5 mol% of rutile TiO_2 significantly improved hydrogen absorption kinetics. Pandey et al. [18] showed also that the particle size of TiO_2 is a very important factor. They have obtained the lowest hydrogen desorption activation energy for 50 nm particles. According to Croston et al. [15] a reduction of the Ti^{4+} in TiO_2 to metallic Ti appears to result in the formation of the active species responsible for catalyzing the MgH_2 dehydrogenation reaction. It is worth mentioning that all findings are related to bulk materials.

Concerning the TiO_2–H interaction, Yin et al. [19] have investigated hydrogen coverage on TiO_2 (110) surface under different experimental conditions of exposure to atomic hydrogen. They obtained maximum H monolayer coverage on TiO_2 (110) surface of only 70% at room temperature, regardless of applied partial pressure of hydrogen. The same group confirmed that during the heating of the hydrogenated sample H atoms have migrated into TiO_2 bulk. This is unusual behavior since desorption of H_2 (or H_2O) molecules into the gas phase is a common characteristic of hydroxylated oxide surface. These results were confirmed by Kowalski et al. [20]. Filippone et al. [21] carried out research which showed that hydrogen behaves as a deep donor in rutile phase and forms an OH^+ complex by an interaction of H atom with oxygen vacancy, where H formed bonds with a prevailing ionic character. They have shown also that electronic localization effects in the bulk TiO_2 call for the addition of the Hubbard-like term to properly describe bonding and changes in charge distribution after hydrogen incorporation. Moreover, the formation of Ti^{+3} species due to the localization of H and OH^+ electronic levels on some Ti neighbors, support the idea that hydrogen atoms are adsorbed as protons onto outer oxygen atoms.

As shown by microstructural analysis provided by Cui et al. [22], nano-sized layer of TiO_2 with nano-grains of less than 10 nm cover the surface of Mg. In this kind of structure, multiple-valence Ti not only acts as a catalyst but also forms many interfaces with Mg/MgH_2. They have shown that TiO_2 covers the surface of MgH_2 particles even after 10 cycles. According to Polanski et al. [12] the decomposition enthalpies of composites are not affected by the introduction of nano-sized TiO_2 so there is no oxide reduction to pure metal.

Even though a large number of recent papers claim the catalytic activity of both Ti and TiO_2 to enhance the (de)sorption of hydrogen in MgH_2 the atomic-scale role of them is still not clear. In particular, the role of oxygen in H desorption is an open question, as well as its interaction with extended systems like interfaces. In our previous papers [23–25] a detailed study of the H desorption near an interface has been addressed taking into account explicitly the presence of a dopant (both Fe and Ni). A detailed description of ab-initio molecular dynamics (MD) simulations has been provided to study a reliable MgH_2–Mg interface at different external temperatures: from room temperature to 900 K. In this range of temperatures the model proposed by authors describes accurately the hydrogen desorption along the interface due to the structural deformation induced by the dopants. The computed desorption temperature is in very good agreement with the experimental indications.

Although any of aforementioned (de)sorption steps could be rate-limiting, we have focused on hydrogen mobility (as a measure of diffusion) through the hydride-metal interface in the presence of Ti and TiO_2 dopants. In this paper, by using the model of the MgH_2–Mg interface, previously developed and already tested against experimental and numerical results, the effect of both Ti and TiO_2 is studied to characterize the atomic-scale destabilization and its effect on hydrogen desorption. The results of numerical investigations of both Ti and TiO_2 substitutional doped interface system MgH_2–Mg are presented. The changes in hydrogen dynamics as consequence of Ti and TiO_2 doping in the vicinity of MgH_2–Mg interface are explored, by means of full structural relaxation, details of the electronic structure and charge density and Car–Parrinello molecular dynamics.

The computational details are illustrated in Section 2, while the physical systems constituted by the MgH_2–Mg interfaces and dopants are described in Section 3. In Section 4 the systems at the end of the ionic relaxations are analyzed, together with the temperature dependence of the hydrogen mobility and the structural analysis of the interfaces. To fully characterize the interface a discussion on the details of electronic properties is reported in Section 5. Properties of charge density topology of bulk MgH_2 doped with TiO_2 were assessed to explain observed differences in the doping mechanism of Ti and TiO_2.

2. Computational details

CPMD (Car–Parrinello Molecular Dynamics) code [26,27], based on plane-wave/pseudopotential implementation of Density Functional Theory (DFT) [28,29], has been used to perform both ionic relaxations and molecular dynamics calculations. Troullier–Martins norm conserving pseudopotentials [30] for magnesium, hydrogen, titanium and oxygen together with Perdew–Burke–Ernzerhof (PBE) [31] approximant GGA exchange–correlation potential were used [32,33]. Magnesium pseudopotential with semicore states was chosen in order to assure high accuracy in the energy evaluations (see for example [34]). The electronic wave functions were expanded in a plane-wave basis set with a kinetic energy cut-off equal to 1090 eV. The supercell approximation has been used to attain large–scale molecular dynamics simulation to model a reliable interface. Periodic boundary conditions (PBC) have been used to simulate an infinitely extended system.

Two commensurate surfaces, one for Mg and one for MgH_2, has been selected to fulfill a simulation cell with PBC. Such a constraint narrows the possibilities of finding two free surfaces for a proper interface. Among the low Miller index surfaces of both materials, it is found that the MgH_2(110) surface is nearly commensurate to either Mg(010) or Mg(100) surfaces, according to periodic boundary conditions, by minimizing the lattice mismatch. Following the numerical procedure developed in previous studies [23–25], the