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Ni-doping effect of Mg(0001) surface to use it as a hydrogen storage material

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ABSTRACT

A detailed study of Ni-doped Mg(0001) surface performed by PAW method and the gradient corrected density functional GGA-PBE within the framework of generalized Kohn–Sham density functional theory (DFT) is presented in this work. Structural and electronic properties of magnesium surface interaction with nickel for the purpose of such compounds use for creation of hydrogen storage matrixes were investigated here. Choice of the PBE functional was caused by the good accordance of its prediction of the cell parameters with experimental results. It was shown that Ni atoms prefer to substitute for Mg atoms. Using NEB method, the diffusion barrier was calculated, and the most probable reaction path was established. In particular, when the Ni atom dopes the magnesium surface, it can migrate to the bulk and substitute for Mg in subsurface layers. Also a possibility of nickel cluster formation on clean surface of magnesium was examined. The kinetic factors hinder the movement of the nickel atoms to each other and make problematic the formation of clusters. The studies presented here showed that the diffusion barriers of the nickel atom migration from the cluster on the surface to the bulk of magnesium are 1.179 eV and 1.211 eV for the forward and reverse reactions, respectively. Therefore an improvement of the hydrogenation properties of Ni-doped magnesium surface depends on deposition not of the individual atoms, but their clusters. Hydrogenation of Ni cluster doping the magnesium surface was investigated. Initially Kubas complexes arise on the Ni cluster with hydrogen–hydrogen bond lengths equal to 0.80–0.87 Å. Next the cluster needs to be saturated by hydrogen atoms to allow them later to migrate from cluster to magnesium.

1. Introduction

In the new century society needs highly efficient transport utilizing the renewable and clean energy. Use of hydrogen is a possible way to meet future energy needs of the population because this is the most widespread element in the universe, and it contains the highest energy density and can be burned clean, producing water only. Therefore hydrogen has great potential for wide use in the energy sector, particularly as a fuel for vehicles. The US Department of Energy (DOE) published technical system targets for hydrogen storage applications relative to light-duty fuel cell vehicles. The predicted minimum hydrogen storage capacity here should be 5.5 wt% and 40 g/L at the operating ambient temperature between −40 and 60 °C [1]. Also low temperatures of hydrogen desorption and low pressures of hydrogenation are required. Furthermore, the financial cost and toxicity properties of storage materials need to be carefully considered before realization of their practical use.

Hydrogen storage in a solid state phase offers several benefits as compared with other means of storing hydrogen. MgH_2, AlH_3, $NaAlH_4$, LiH and other metal hydrides can be used as a matrix for hydrogen storage with varying success. Magnesium is one of the most promising metals in this set, because it has low cost, low molecular weight, availability and non-toxicity.

However, there are some serious challenges to use magnesium as reversible sorbent. Most of them are associated with the occurrence of diffusion limitations in magnesium hydride, where hydride phase formed initially creates a "surface shield" that blocks further hydrogen sorption [2]. This delays diffusion of the hydrogen atoms into the bulk of metal. Furthermore, there is a strong ionic Mg–H bond in magnesium hydride, which is caused

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by a relatively high enthalpy of formation ($\Delta H = -75$ kJ/mol). This bond leads to the increase of the temperature of hydrogen desorption out of the hydride phase and as a result to the decrease of a rate of this process [3]. Finally, the high barrier of the hydrogen molecules dissociation on the magnesium surface is another problem [4–7]. Therefore using magnesium and magnesium hydride in a pure form is not possible. However, the particle size reduction is the promising way to overcome challenges.

In recent years, special attention is paid to magnesium nanoparticles due to their novel properties different from those of bulk materials [8–11]. Usually, nanoparticles are prepared by two main methods such as milling in a ball mill and gas phase condensation [6,8,11]. It should be noted that there are some other methods of nanoparticles synthesis such as the preparation in tetrahydrofuran by the reduction of the lithium magnesium salt [12] and as the sonoelectrochemical method which is based on the use of ultrasound [13]. Another modern approach of the preparation of ultrafine nanoparticles of magnesium (size about 40 nm) is the arc melting of magnesium in the acetylene plasma [14]. The application of these methods reduces the particles size of magnesium, and improves the diffusion and kinetics of the hydrogenation/dehydrogenation of Mg nanoparticles.

At the same time it is advisable to consider the possibility of magnesium modification by various transition metals. Numerous studies are aimed at overcoming kinetic limitations by adding a catalyst to increase the rate of hydrogen dissociation on the magnesium surface [2,15]. The most of studies published previously show the improvement of the absorption/desorption reaction kinetics at addition of transition metals. However, the mechanism of such reactions remains obscure. An implementation of one or another mechanism is dependent on many conditions such as the deposition temperature, the rate of atoms feed and other factors. The determination of these mechanisms is experimentally difficult or extremely resource-expensive. In this situation the quantum-chemical methods seem preferable to study the processes occurring in the systems during these reactions.

The barriers of the hydrogen dissociation on the transition metals atoms, which were situated on the magnesium surface, were theoretically calculated earlier [16–20]. Du et al. [18] have shown that using of titanium as the modifying component makes such barrier quite low. However, titanium forms a strong stable hydride bond, which, to be broken, requires a lot of energy. Therefore diffusion of these two dissociated hydrogen atoms into the bulk of magnesium is very complicated [19]. Palladium as catalyst makes dissociation quick, and diffusion from palladium into the bulk of magnesium is not difficult [18]. Unfortunately, this metal possesses effective catalytic activity as compared with nickel and titanium only at high temperatures. On the other hand, Pozzo and Alfè [20] have investigated the dissociation and the followed diffusion of the hydrogen atoms on the magnesium surface (0001) modified by the different transition metals (Ti, V, Zr, Fe, Ru, Co, Rh, Ni, Pd, Cu, Ag). The results showed that insertion of the atoms Fe, Ni, Rh, and (to some extent) Co and Pd can lead to the low hydrogen dissociation and diffusion barriers, but the most effective alloying component is Ni. Experimental results confirm these theoretical conclusions. In other words hydrogenation occurs quickly and efficiently in magnesium doped by nickel. However, despite the experimental development and theoretical approaches to overcome the restrictions of the use of magnesium, including its modification by transition metals, its practical use as the hydrogen storage matrix remains problematic.

According to the theoretical and experimental results [16–23] it can be assumed that the following processes can occur due to the nickel adsorption precipitation on the magnesium surface: clustered and epitaxial growth of transition metal on the surface, inclusion of d-metal atoms into the metal-sorbent lattice interstices, placement of transition metal atoms into the vacancies, formation of the intermetallic compound. In this case, an essential step in the interaction mechanism determination of transition metal with magnesium is detailed consideration of these processes and description of compounds that are generated on the surface and the subsurface layers depending on the synthesis conditions.

In the present study, the low index magnesium surface Mg(0001) has been studied computationally with help of DFT method. The behavior of nickel atoms at the surface and subsurface layers of magnesium has been investigated by quantum-chemical simulation. A possible reaction pathway for nickel atom diffusion from surfaces into the bulk has been chosen, and its potential barriers have been computed using the nudged elastic band (NEB) method. Next, a possibility of cluster formation and nickel diffusion from cluster into the bulk of magnesium has been examined.

2. Computational method

Quantum-chemical calculations were performed with the Vienna *ab initio* simulation package (VASP) [24–27] and within the density functional theory (DFT) [28,29]. The Perdew–Burke–Ernzerhof functional was used for the calculation of the exchange–correlation energy [30]. The electron–ion interactions were described by the projector augmented wave (PAW) method [31]. The plane wave cutoff energy for all calculations was set at 400 eV. An energy difference of 10^{-4} eV was set as the convergence criterion between successive ionic steps during the geometries relaxation.

The equilibrium geometry of the magnesium unit cell with the space group symmetry P63/mmc has been calculated at the work initial stage to study the interaction of the Mg surface with atoms and clusters of nickel. The *k*-point samplings of the first Brillouin zone (1BZ) have been chosen as $12 \times 12 \times 12$ according to the Monkhorst–Pack scheme [32]. It was detected that these values are sufficient for a correct description of the lattice parameters (calculated values of a and c are 3.10 and 5.00 Å, when experimental values are 3.22 and 5.23 Å [33], respectively).

The investigation of the processes on the surface was the following stage, where a slab consisting of the hexagonal cells with surface index (0001) and translation vector of 3.10 Å was used in the calculations. The structures with a different number of layers were examined to find the optimal thickness of the slab. It was detected that difference of a surface energy density between the slabs containing of 7 and 8 layers, respectively, is less than 0.01 eV/Å. Thus the seven atomic layers is enough thickness of the slab for the accurate modeling of the surface processes, therefore this model was used for the next steps of the investigation. A vacuum space was equal to 15 Å to guarantee a sufficient separation between the periodic images.

Using the optimized slab geometry, a supercell with a size of $7 \times 7 \times 1$ of the unit cells of the slab was modeled to exclude an interaction of the nickel atoms between neighboring images. The *k*-point samplings of the first Brillouin zone (1BZ) were chosen as $2 \times 2 \times 1$. In the case of the surface processes' simulation four different positions of the Ni atom were examined: above the Mg atom (top), above the Mg–Mg bond (bridge), above the tetrahedral (hcp) and octahedral (fcc) hollows (Fig. 1(a–d)). In the case of a penetration the nickel atom was placed into the tetrahedral and octahedral hollows of the surface layer (Fig. 1(e and f)). Also a substitution of the Mg atom in the first, second and third layer by the Ni atom was examined (Fig. 1(g–i)).

3. Results and discussion

The specific binding energies of supercell with nickel atoms at the doping and the substitution (Table 1), respectively, were defined as

$$E = \frac{E_T - E_S - nE_{Ni}}{n}, \quad (1)$$

$$E = \frac{E_T - E_S - nE_{Ni} + nE_{Mg}}{n}, \quad (2)$$

where E_T is the total energy of the magnesium supercell with n atoms of nickel, E_S is the energy of the magnesium supercell separately, E_{Ni} is the energy of the Ni atom in its bulk crystal structure, E_{Mg} is the energy of the Mg atom in its bulk crystal structure.

According to the specific binding energies the most stable structures are those where the magnesium atoms are replaced by the nickel atoms. However, there is no substitution solution at the