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## Hydrogen adsorption on Pd/TiFe (110) surface

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### Abstract

Adsorption of hydrogen on the TiFe (110) surface covered by palladium monolayer was investigated using the full potential linearized augmented plane wave method within the local density approximation. Influence of palladium coating to adsorption properties of the TiFe (110) surface as well as difference it from Pd/TiFe (100) are discussed.

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### 1. Introduction

The TiFe alloy is an excellent material for hydrogen storage [1]. However, the surface of this alloy is very corrosive and requires an initial activation for increase of adsorption capability. A possibility to overcome the problem of diminution of sorption capacity is to coat the surface by an anti-corrosive layer, which is permeable for hydrogen. The formation of surface oxide layer can be prevented by the usage of a thin layer of palladium as coating [2]. In order to understand the adsorption of hydrogen on the Pd covered TiFe surface at the microscopic level it is necessary to investigate the electronic structure (ES) of clean TiFe surfaces and its change with influence of palladium and hydrogen.

In our previous papers [3,4] we studied the ES of clean TiFe (001) and (110) surfaces and TiFe (001) covered by Pd monolayer. The different hydrogen geometries and adsorption energies at these surfaces were also studied. We showed that hydrogen adsorption is preferable on the Ti-terminated (001) surface. The Fe-bridge position for hydrogen was

found to be the most stable one among four adsorbate geometries considered onto (110) surface. We found that the changes in the surface ES are connected with hybridization of hydrogen s-states and d-states of surface and subsurface metal atoms. In the presence of Pd coating on the TiFe (001), iron valence band shifted towards the Fermi level ( $E_F$ ), which leads to surface highly reactivity, so adsorption is easier for Pd coating (001) surface than clean TiFe(001). As a continuation of our studies, we investigate hydrogen adsorption on the TiFe (110) with Pd monolayer in order to find microscopic explanation of chemical bonding on this surface and understand the difference in it with studied surfaces.

### 2. Computational details

The FLAPW method (WIEN implementation [5]) within the local density approximation for the exchange-correlation potential was applied to ES calculations of B2-TiFe (110) surface with the monolayer of Pd. Using the supercell technique, the clean surface was simulated by repeated five layers slabs separated in the [110]-direction by vacuum regions. The thickness of the vacuum region corresponding to approximately two bulk lattice spacings was found to be

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sufficient to avoid interaction of the atoms on the surfaces. The lattice parameter was set to the experimental lattice constant  $a = 2.976 \text{ \AA}$  for the bulk TiFe alloy. The multipole expansion of the crystal potential and electron density inside the muffin-tin spheres was cut at  $l = 10$ . Non-spherical contributions to the crystal potential within the MT spheres were considered up to  $l_{\text{max}} = 4$ . The electron energy spectrum was calculated at 24  $k$ -points in the irreducible part of the two dimensional Brillouin zone. The idealized B2-TiFe (110) surface is a rectangular lattice with the same stoichiometry content as in the bulk. In this case the Pd monolayer has almost the same lattice parameters as TiFe (110) surface (2.749 and 3.887  $\text{\AA}$ ). There are two ways to cover the (110) surface by palladium—Pd is above Ti and Pd is above Fe. These variants are denoted as Pd/TiFe and Pd/FeTi, respectively. Initially hydrogen was placed a little bit higher (0.3  $\text{\AA}$ ) above the center of rectangular lattice of Pd. So it was above Ti or Fe depending of Pd type coating.

### 3. Results and discussions

Total and layer-resolved density of states (DOS) of Pd covered TiFe (110) film in comparison with those of clean TiFe (110) are shown in Fig. 1. The Fermi level, as in the bulk, is located in the deep valley of total DOS for both considered cases. This factor is the reason of high adsorption capability of TiFe alloy. Comparison of DOS of Pd-covered and clean surfaces shows that the influence of Pd is appreciable only on the first layer of TiFe (110). The strong splitting of the main peak of TiFe (110) surface DOS at  $-1.3 \text{ eV}$  that is associated with Fe d-states is observed in Pd/FeTi (110) case. The surface DOS shape of palladium

that has a main peak near Fermi level in clean Pd (110) is changed dramatic. It shifted downwards from  $E_F$  and has the main peaks about  $-3$  and  $-3.2 \text{ eV}$  for Pd/FeTi and Pd/TiFe (110), respectively. It is necessary to note that relaxation of the H and Pd on TiFe fixed substrate does not considerably influence the shape of surface DOS (see Fig. 2) in spite of hydrogen position changes substantially—it is situated under palladium layer after relaxation (for final geometry). Note that the investigation of on clean TiFe (110) surface showed that this surface is rumbled with Ti atoms outwards shift by 0.15  $\text{\AA}$  in comparison to the topmost Fe position and the values of inward relaxation were found equal to  $-14.7\%$  for Fe and  $-7.4\%$  for Ti. In general the changes of DOS and some electron properties was found to be insignificant after relaxation. It is obvious that surface relaxation influences the values of adsorption and binding energies but not the trends which were found for ideal surfaces.

Fig. 3 shows layer-resolved DOS for Pd covered TiFe (110) film with adsorbed hydrogen. In contradistinction to H adsorption on Pd/TiFe (001) surface, the hydrogen states are lying higher in the energy. It is seen that H–Pd interaction leads to shift of H states upwards. The higher location of hydrogen states provide higher reactivity of H on this surface by comparison with H–Pd/TiFe (001).

We calculated the minimum of adsorption ( $E_{\text{ad}}$ ) and binding ( $E_{\text{b}}$ ) energies as a function of distance between hydrogen and the surface Pd layer. It was found that the minimum of adsorption energy  $E_{\text{ad}} = -0.097 \text{ eV}$  when H is situated under palladium monolayer in Ti-top position (2.05  $\text{\AA}$  above Ti) in H–Pd/FeTi (110). In this case  $E_{\text{b}} = 2.47 \text{ eV}$ . We supposed that total adsorbate–substrate relaxation will decrease these values. In our previous paper was shown that Ti-top as well as Fe-top positions

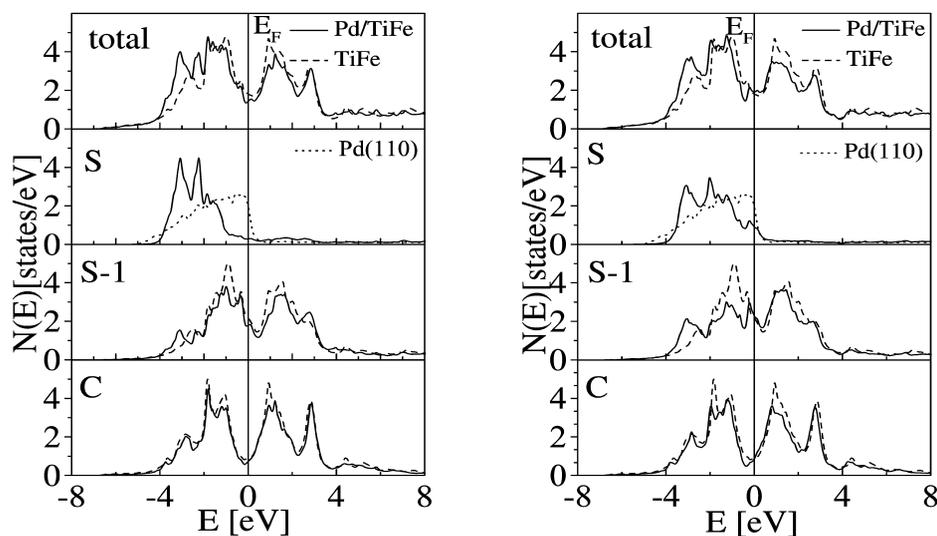


Fig. 1. Total DOS and sum of local DOS's for central and surface layers in TiFe (110) (dashed lines) and Pd-covered TiFe (110) film (solid lines): Pd is above Ti (left); Pd is above Fe (right).

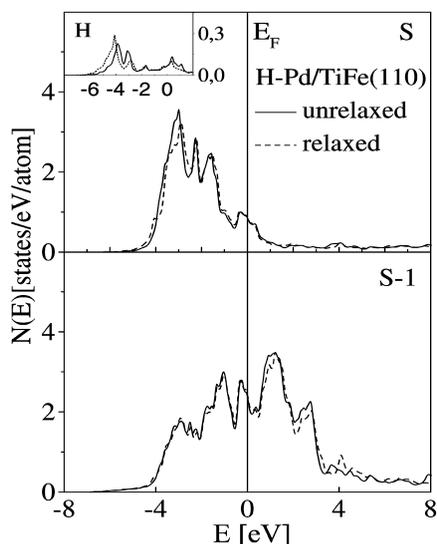


Fig. 2. Local and sum of local DOS's of surface and subsurface layers in H-Pd/TiFe(110).

are not quite good for hydrogen adsorption and Fe-bridge one was found as preferable site for clean TiFe (110) surface. Such location of hydrogen causes a weakening of iron–iron bonds and promote the phase transition in the orthorhombic structure during hydrogenation. Since our results shown that Pd coating is well permeable for hydrogen we think that interaction of H with Pd covered TiFe (110) will be the same as in clean TiFe (110) surface. Moreover, change in shape of Fe band and increasing of surface states near Fermi level in Pd/FeTi (110) make iron

with presence of palladium coating more chemical active than it is in clean TiFe (110) surface.

It is known that desorption properties of TiFe can be improved by partial replacing of iron by nickel [6]. It is interesting to consider critical situation—TiNi alloy in the point of view of interaction of hydrogen with Pd covered TiNi (110) surface. The layer-resolved H-Pd/TiNi (110) DOS are given in Fig. 4. In the presence of hydrogen the Pd states lie slightly deeper in energy than in Pd/TiNi (110) as in Pd/TiFe (110). The ES of subsurface layers H–Pd/TiNi (110) is only slightly different from bulk one as in H–Pd/TiFe (110) when Pd is located above Ti. As in the case Pd/FeTi the changes in the surface ES is more expressed when Pd is above Ni. Sharp *d*-Ni peak is splitting up to three ones. In this case center of gravity of Ni bands lie lower in energy in comparison with bulk. The Pd states are shifted downwards by about 1 eV in comparison with clean Pd (110) but Pd main peak lies close to  $E_F$  than Ni one. Note that the shape of Pd surface DOS in Pd/TiNi (110) changes significantly in comparison with clean Pd (110) as a case when Pd is located above Ti or Fe in TiFe (110). Total DOS structure near the Fermi level changes insignificantly in the above mentioned case. The main difference between Pd/NiTi (110) surface ES and Pd/FeTi (110) is that the surface states induced Pd–Ni bonding lie essentially deeper relative to Fermi level and which may be the reason for a comparatively less TiNi adsorption capability.

So we studied the influence of Pd coating on the surface ES and chemical bonds on TiFe and TiNi (110) surfaces. Our results show that in all considered cases H is located below Pd surface layer after relaxation. Furthermore H try to

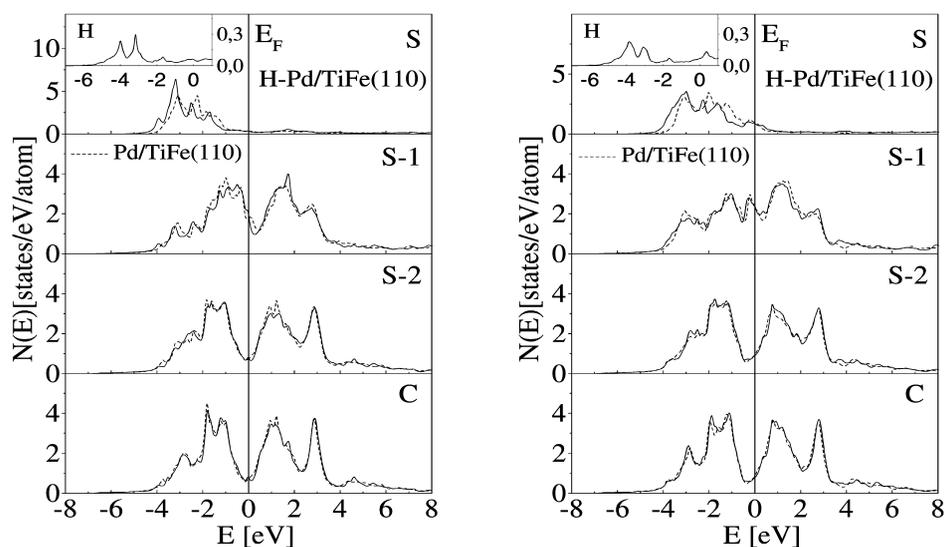


Fig. 3. Local and sum of local DOS's of different layers in H-Pd/TiFe (110) film (solid lines): Pd is above Ti (left); Pd is above Fe (right). H is in the hollow position.

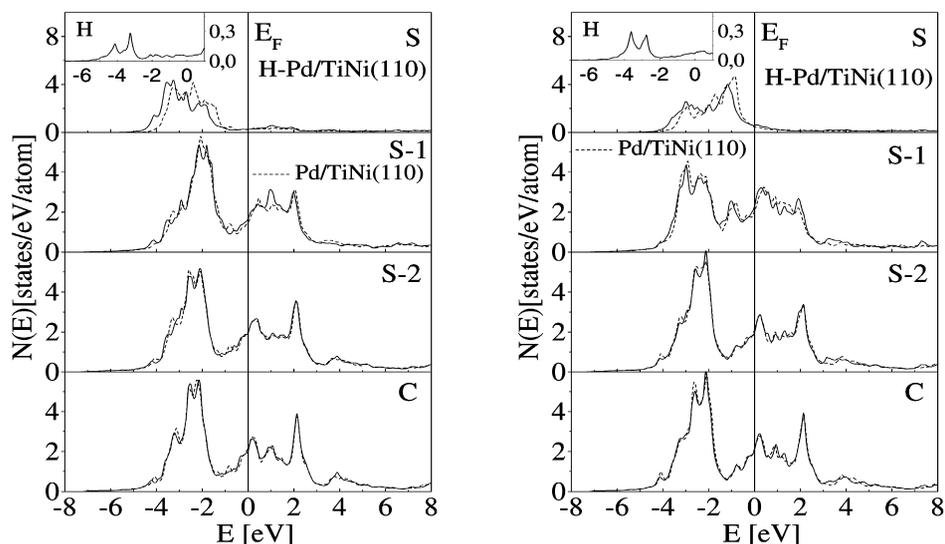


Fig. 4. Local and sum of local DOS's for different layers in H-Pd/TiNi (110) film (solid lines): Pd is above Ti (left); Pd is above Ni (right). H is in the hollow position.

be between Fe or Ni atoms that can cause a weakening of interatomic bonds and phase instability or H-induced phase transformations. The Ni–Ni bond is stronger than Fe–Fe one which can be a reason why the structural transformation differ in TiNi and has less hydrogen adsorption capability. Since Pd coating is well permeable for hydrogen we suggest that the adsorption properties are the same as on clean TiFe (110) surface. Iron with presence of palladium is more chemical active. The present calculations allow to predict the preferable surface orientation and composition but in general the hydrogen storage materials properties are mainly determined by bulk structure instabilities upon hydrogenation.

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