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Svetlana Kulkova,[1,2] Dmitriy Chudinov,[2] Sergey Eremeev,[1,2] and Sergey Kulkov [2]

[1] Institute of Strength Physics and Materials Science of the RAS, Tomsk, Russia
[2] Tomsk State University, Russia

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The Interaction of Simple Adsorbates with TiNi Surfaces [#]

Svetlana Kulkova,[1,2,]* Dmitriy Chudinov,[2] Sergey Eremeev,[1,2] and Sergey Kulkov [2]

[1] Institute of Strength Physics and Materials Science of the RAS, Tomsk, Russia
[2] Tomsk State University, Russia

Abstract

Motivation. We present an *ab initio* investigation of the surface electronic structure of B2–TiNi (001) and (110) thin films with adsorbed hydrogen atoms and with Pd coating. This study can be useful for understanding of electron factors which are responsible for hydrogen adsorption on metal surface and allow to increase surface reactivity by alloying.

Method. The computations were made with the full potential linearized augmented plain wave method. We have used the software WIEN2k, www.wien2k.at.

Results. The adsorption and binding energies are calculated when hydrogen adsorbs on the TiNi or TiFe (001) surface in the "hollow" position. The influence of Pd coating on the surface (001) and (110) electronic structure is discussed. The change of the local electronic structure in the presence of Pd is analyzed in dependence on interfacial atoms or Pd place on the surface.

Conclusions. The hydrogen adsorption is preferable on Ti–terminated B2–TiNi (001) surface as in the case of B2–TiFe (001). It is shown that Pd influences the surface ES significantly when Ni is interfacial atom in the case (001) surface or Pd locates above Ni on TiNi (110). Since Pd coating is well permeable for hydrogen the adsorption properties of Pd–covered and clean TiNi (110) can be the same. The interaction between the H orbitals and the metal d–states depends strongly on the adsorption geometry. The present results are very important for understanding of microscopic origin of the metal alloys surface reactivity. The calculations allow to predict the preferable surface orientation and its composition.

Keywords. Transition metal alloys; surface and interface; electronic structure.

Abbreviations and notations	
BCT, body centered tetragonal	FCC, face centered cubic
DOS, density of states	FLAPW, full–potential linearized augmented plane wave
E_{ad}, adsorption energy	LDA, local density approximation
E_b, binding energy	N(EF), density of states at the Fermi level
EF, Fermi level	TM, transition metal
ES, electronic structure	ϕ, work function

1 INTRODUCTION

In the past two–decade the adsorption properties of metal surfaces have been a subject of an

increasing number of both experimental and theoretical studies. However, up to now not sufficient attention has been paid to the study of the surface electronic structure (ES) of transition metal (TM) alloys. Ti–based alloys with 3–5d TM have important technological properties such as the shape memory effect, the high hydrogen capacity, etc. They are also found widespread application in medicine as implant materials. TiFe and TiNi are considered as key materials for hydrogen storage and the development of future clean hydrogen energy systems. Despite of intensive experimental investigations the modification of surface electron properties by hydrogen adsorption remains an open question. The other problem is connected with the formation of surface oxide layers, which hinder the hydrogen adsorption. The experimental studies of TiFe showed that the formation of surface oxide layers can be prevented by the usage of Pd coating. It should be interesting to compare the adsorption characteristics in the set TiFe–TiNi–TiPd in order to explain in the microscopic level the high surface reactivity and hydrogenation capability of Ti–based alloys. In our previous works [1,2] we investigated electronic structure of some Ti–based alloys surfaces and the hydrogen adsorption on $B2$–TiFe (001) and (110) surfaces. As a continuation of our studies, we investigate hydrogen adsorption in the $B2$–TiNi thin films. The study of the hydrogen adsorption on Pd–covered TiNi surfaces is also carried out.

2 COMPUTATIONAL DETAILS

The full potential linearized–augmented–plane–wave (FLAPW) method [3] within the local density approximation (LDA) for the exchange–correlation potential was applied for calculations of the electronic structure for clean $B2$–TiNi surfaces as well as with hydrogen or oxygen in the fourfold "hollow" site. Using the supercell technique, the surface was simulated by repeated 5–9 layers slabs separated in one direction by a vacuum region ~10 Å. The lateral lattice parameter was set to the experimental one (a = 3.015 Å). The work function was determined as the difference between the vacuum level and Fermi energy (EF). The vacuum level is found from the self–consistent potential in the middle of the vacuum region. The binding energy has been defined as E_b = 1/2($E_{H/substr}$–E_{substr}–2E_H). Here E_H is the energy of free hydrogen atom, and "E_{substr}" means total energy of clean TiNi (001) film. The adsorption energy was calculated as E_{ad} = 1/2($E_{H/substr}$–E_{substr}–E_{H2}), where E_{H2} is total energy of hydrogen molecule. In our estimations we used experimental values of E_H = –13.6058 eV and E^b_{H2} = –4.75 eV (E^b_{H2} is the binding energy of H_2 molecule). More details of calculations can be found in [1,2].

Table 1. Adsorption and binding energy in eV, the height (h_0) of the stable adsorption site above the surface layer in Å. The values in parentheses are given for the unrelaxed surfaces

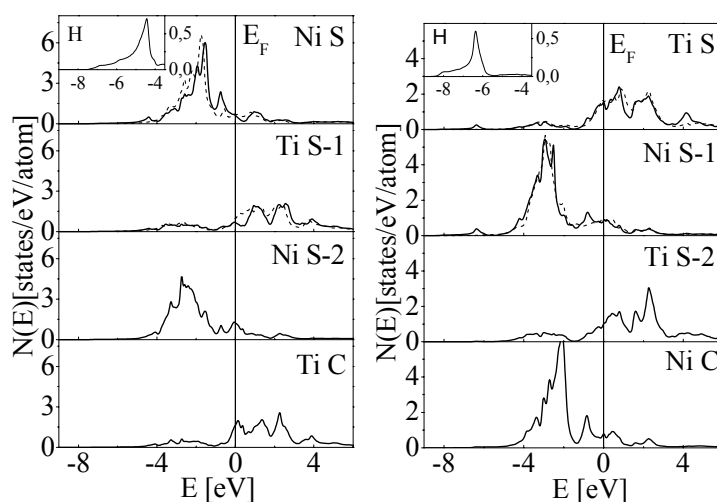|	E_{ad}	E_b	h_0
H–Ti/TiNi (001)	−0.88 (−0.81)	−3.25 (−3.19)	0.46 (0.31)
H–Ni/TiNi (001)	−0.67 (−0.72)	−3.05 (−3.10)	0.65 (0.31)
H–Ti/TiFe (001)	−0.75 (−0.78)	−3.12 (−3.15)	0.48 (0.31)
H–Fe/TiFe (001)	−0.73 (−0.97)	−3.09 (−3.30)	0.76 (0.31)
FM H–Fe/TiFe (001)	−0.56 (−0.72)	−2.94 (−3.09)	0.74 (0.31)
H–PdTi/NiTi (001)	−0.45 (−0.41)	−2.82 (−2.78)	0.44 (0.31)
H–PdNi/TiNi (001)	−0.92 (−0.86)	−3.29 (−3.24)	0.19 (0.31)
H–PdTi/FeTi (001)	−0.25 (−0.12)	−2.62 (−2.49)	0.37 (0.31)
H–PdFe/TiFe (001)	−0.47 (−0.45)	−2.85 (−2.83)	0.23 (0.31)

Figure 1. Layer resolved DOS of H–covered TiNi(001) films: a) Ni–terminated TiNi (001), b) Ti–terminated TiNi (001).

3 RESULTS AND DISCUSSION

Hydrogen atom was placed in the fourfold "hollow" position on the *B*2–TiNi (001) surface. The preference for the fourfold "hollow" position on the *B*2–TiMe (001) alloy surface for the hydrogen adsorption is related to the higher coordination number at this site, and to the minimization of the repulsion between the overlapping charge densities of H atoms with the surface and subsurface atoms. It should be noted that within the LDA we found a surprisingly strong contraction of the interlayer distance between the surface and subsurface layers, –20.1% for Ni/TiNi(001) and –14.9% for Ti/TiNi(001). In addition to a relaxation of a clean surface we found a minimum of the adsorption energy, which was calculated as a function of the distance between the H atom and the surface layer. Unfortunately we did not perform the final relaxation of the adsorbate/substrate complex because it takes a large computational time with our approach and does not change significantly the results. The lower values of inward relaxation were obtained in the case TiNi (110). They are –15.2% for Ni and –7.4% for Ti. The equilibrium positions of hydrogen on both Ti– and Ni–terminated TiNi (001) surfaces (Ti/TiNi and Ni/TiNi) are given in Table 1. The minimum of

total energy for Ti/TiNi is observed at a distance of 0.46 Å from surface layer (1.74 Å from subsurface Ni atom – close to the distance of the H–Ni bond length). In the case of Ni–terminated surface the value of H–Ti distance is 1.86 Å. Calculated binding and adsorption energies for relaxed geometry are given in Table 1. As seen the adsorption of hydrogen is more preferable on the Ti–terminated (001) surface. Such tendency was observed for TiFe (001) surface as well, but in the last case the preference of Ti–terminated surface for hydrogen adsorption is only due to the magnetism of Fe surface layer that increase E_{ad} by about 0.2 eV. In our case both terminations of TiNi (001) surface are non–magnetic. Note that the adsorption energy is very sensitive to the surface relaxation and the relaxation influences the electronic structure only for the first two surface layers.
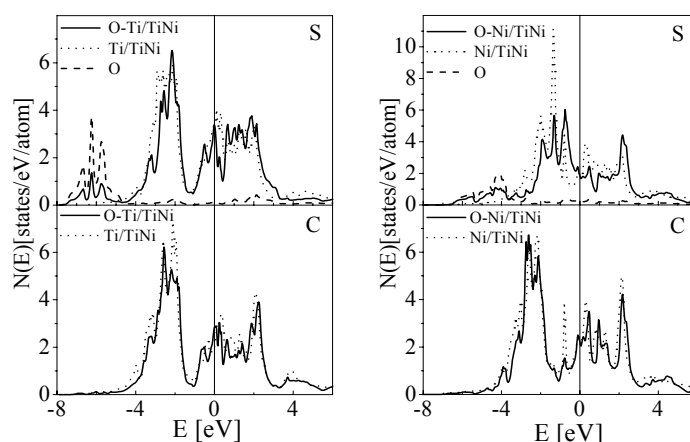

Figure 2. DOS for O–covered Ti/TiNi and Ni/TiNi (001) surfaces for suface and bulklike layers are given in comparison with clean *B*2–TiNi (001) surfaces.
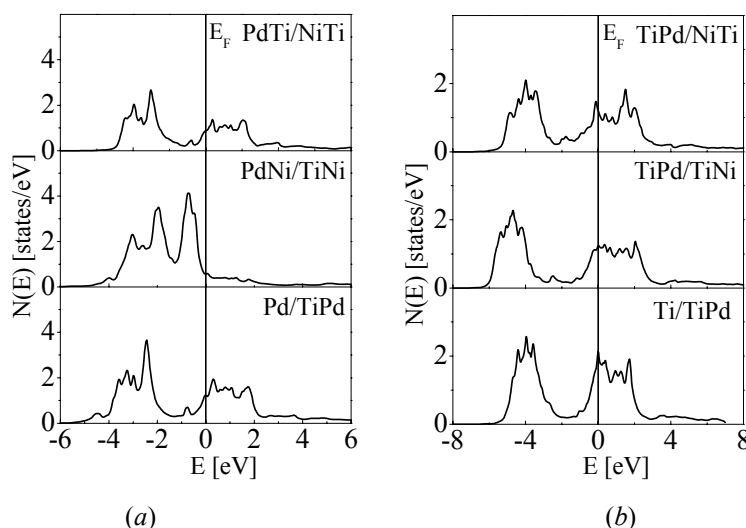

(a)   *(b)*

Figure 3. The surface DOS for both terminations of B2–TiNi (001) with Pd in surface (*a*) and subsurface (*b*) layer in comparison with results for B2–TiPd (001).

The local DOS's in the adsorbed H layer and in the surface and two subsurface layers of TiNi

(001) surface as well as in the central layer, compared with the layer–resolved DOS's of the clean TiNi (001) for both surface termination, is shown in Figure 1. H–metal bonding states appear below the d–band bottom of the clean TiNi surface. The hydrogen 1s states are located at around –4 eV below EF for the Ni–terminated surface and they lie deeper at –6 eV for the Ti–terminated case. It should be noted that the hybridized states of hydrogen with surface Ti and with subsurface Ni for H–Ti/TiNi as well as H–Ni bonding states for H–Ni/TiNi are appeared. Partial DOS's give us the opportunity to find states, which are responsible for this hybridization. The binding in the fourfold "hollow" position occurs in H–TiNi (001) through the $s–d_{xy}$ hybridization of hydrogen and titanium (nickel) surface states as well as $s–d^3z^2–r^2$ hybridization of hydrogen and subsurface nickel (titanium). Hydrogen can influence to central layer states only indirectly through the hybridization with neighboring atoms. The charge density distribution shows that the region of relatively high electron density is observed from the H site to the Ni one. This occurs despite the fact that the Ti atom is the nearest neighbor of H in the Ni/TiNi(001). We estimated work function (ϕ) for both Ti and Ni surface terminations. The hydrogen adsorption leads to decrease of ϕ values by 0.2 eV (4.29 eV – 4.09 eV) for Ti/TiNi and slightly change ϕ (5.04 eV — 4.97 eV) for Ni/TiNi. This means that surface potential changes more sufficiently in Ti/TiNi structure due to preferable H–Ni hybridization in normal direction. Since TiNi (001) film is non–magnetic one the oxygen adsorption can only induce small polarization on the Ni atom in contrast to TiFe case. Our results suggest the possibility of O–induced reconstruction of Ti–terminated TiNi (001) surfaces (Figure 2). In general, oxygen forms a much stronger bond to the TiMe surface than hydrogen and it can block considered "hollow" adsorbate site for H adsorption. The magnetism induced by the oxygen adsorption as in TiFe case can hinder the hydrogen adsorption also. The consideration of oxygen adsorption in the same "hollow" position on TiNi (001) surface shows that the Ni surface states are much more affected due to oxygen chemisorption and the adsorbate *p*–orbitals mix with them. Oxygen adsorption in the "hollow" site slightly increases DOS at the Fermi level for Ti–terminated surface and does not change N(EF) for Ni–terminated surface whereas the DOS profile changes drastically especially for Ni/TiNi case. Our results show that Ti–terminated TiNi (001) surface is unstable in respect to O adsorption whereas Fe–terminated surface was unstable in the case TiFe (001) film. In order to prevent the formation of surface oxide layer in TiFe the thin layer of Pd as a cover can be used. We considered the influence of Pd on the hydrogen adsorption for TiFe (001) in our previous paper [4]. It is known that desorption properties of TiFe can be improved by partial replacing of iron by nickel. It is interesting to consider critical situation – TiNi alloy in the point of view of hydrogen interaction with Pd–covered TiNi (001) and (110) surfaces. The lattice parameter for FCC Pd is 3.887 Å and 2.749 Å for conventional BCT lattice that gives the mismatch with B2–TiFe and TiNi lattice parameter by –7.6 % and –8.8 %. On the other hand the lattice parameter of B2–TiPd (3.18 Å) is greater by 6.9 % and 5.5 % than that of B2–TiFe (2.976 Å) and TiNi (3.015 Å). Titanium as Pd is an element, which also actively adsorbs hydrogen. Upon hydrogen loading TiFe

forms several phases: orthorhombic $TiFeH_{1.37}$ and monoclinic $TiFeH_2$. The structure of TiNiH was established as tetragonal one corresponding to the space group I4/mmm. The structures of the hydrides $TiNiH_x$ with $x = 1.0$ and 1.4 have been resolved in [6].

We carried out the investigation of ES for different substrate compositions in Pd–covered TiNi (001) system. DOS's of Pd–covered TiNi (001) are presented in Figure 3 in comparison with clean TiPd (001). We also analyzed changes of ES during hypothetical Pd segregation. Results are given in Figure 3 (right). The influence of Pd is restricted to two upper layers. It is obvious, that in the case of thicker Pd coating the absorption properties of the system would be similar to pure Pd. In the case of PdNi/TiNi (001) when Ti surface atoms are replaced by Pd atoms ES changes significantly in the surface layer, because bands of Pd are located below EF in the same energy region as Ni bands (Figure 3*a*). Palladium strongly disturbs Ni states and shifts them towards EF. The value of N(EF) slightly decreases for Ni subsurface layer from 1.08 down to 0.82 states/eV/atom. In PdFe/TiFe N(EF) increases for Fe subsurface layer from 1.16 up to 3.8 states/ eV/atom. At the same time the value of N(EF) for both surface and subsurface layers in PdFe/TiFe increases considerably from 1.35 up to 2.45 states/eV/atom. As it was shown this electron factor is favorable for gas absorption. DOS of PdNi/TiNi is shifted from EF in comparison with one for PdFe/TiFe (001) and N(EF) decreases considerably in comparison with clean Ti/TiNi (0.57 and 1.72 states/eV/atom, respectively). Introducing Pd on Ni site we found that Pd–states are placed significantly lower in the energy in comparison with Ni states in Ni/TiNi (001) as well as Pd states in Pd/TiPd (001). Titanium bands located at the same position relative to EF than that for Ni/TiNi (001) and Pd/TiPd (001) surfaces. Ti–states are dominant at EF in PdTi/NiTi. In this case the value of N(EF) decreases in comparison with pure Pd/TiPd (001) (0.89, 1.23 states/eV/atom). For PdTi/NiTi (001) system we have 0.45 and 1.30 states/eV/atom at the Fermi level for surface Pd and subsurface Ti atoms, respectively. These values are slightly less than one for PdTi/FeTi (001) system. We calculated the work function for PdNi/TiNi and PdTi/NiTi (001) surfaces and obtained 4.95 eV and 4.90 eV, respectively. These values are less in comparison with ϕ for clean Pd (001) (5.22 eV – experiment). The values of 5.18 (5.11) eV and 5.07 (5.02) eV were calculated for PdFe/TiFe and PdTi/FeTi (001), respectively. The values in parentheses are obtained for equilibrium geometry. The results with Pd in subsurface layer are given in Figure 3b. As expected the DOS's structures are very similar to that for Ti–terminated TiPd (001) film. In this case, the formation of surface TiPd alloy is possible. In TiPd/TiNi case Pd states are slightly shifted in lower energy region and Ti states are dominant at EF. In both cases N(EF) decreases from 2.13 states/eV/atom for Ti/PdTi (001) down to 1.25 states/eV/atom for TiPd/TiNi (001) and 1.19 states/ eV/atom for TiPd/NiTi (001) surfaces. Because Ti states are highly reactive the formation of the surface oxide layers is possible in all cases as on TiNi (001) surface, which will hinder hydrogen adsorption. The local DOS for H–covered Pd/TiNi (001) films are shown in Figure 4. It is seen that hydrogen introduces only minor changes in ES, which was discussed above. The calculated values

of binding and adsorption energies are given in Table 1. The present calculation shows that PdNi/TiNi (001) surface is more reactive even in comparison with PdFe/TiFe case. So, the hydrogen storage properties depend not on surface reactivity only but the possibility to form bulk hydrides or to be unstable upon hydrogen absorption.
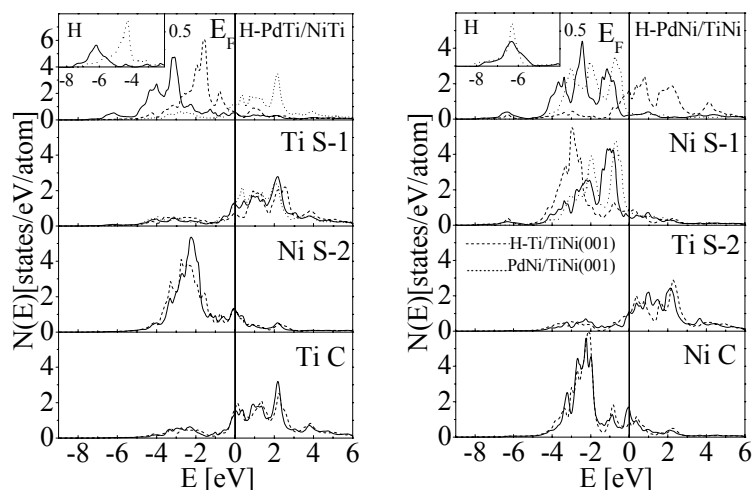

Figure 4. Layer resolved DOS for H–covered PdTi/TiNi and PdNi/NiTi (001) in comparison with results for Pd–covered films and H–covered TiNi (001) films.
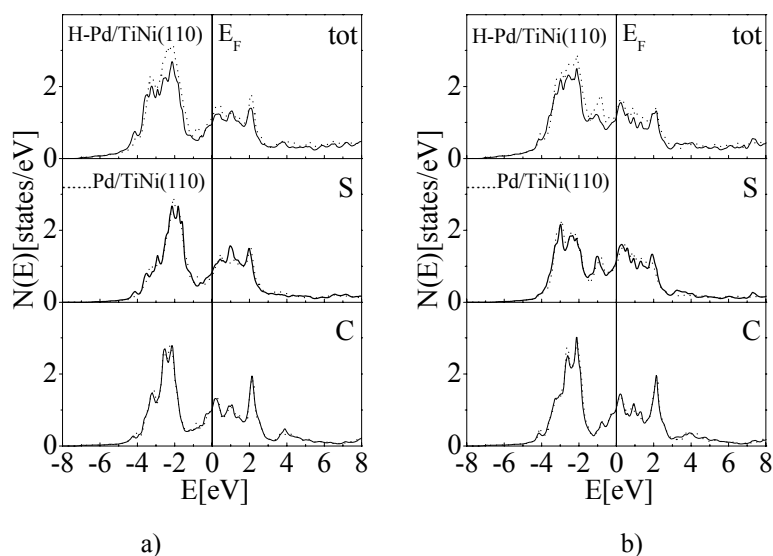

Figure 5. Total DOS and sum of local DOS for surface and central layers in Pd/TiNi(110) (dashed lines) and H–covered Pd/TiNi(110) film (solid lines): a) Pd is above Ti; b) Pd is above Ni.

Let us consider now the hydrogen interaction with Pd covered TiNi (110) surface. We will analyze two possibilities when Pd is located above Ni or Ti atoms. Hydrogen is considered in "hollow" position. H–Pd/TiNi (110) DOS's are given in Figure 5. In presence of hydrogen the Pd states lie slightly deeper in energy than that in Pd/TiNi (110) as in Pd/TiFe (110). The electronic structure of subsurface layer of H–Pd/TiNi (110) slightly differs from bulk–like (C in Figure 5) one

as in H–Pd/TiFe (110) when Pd is located above Ti. The changes in the surface ES are more expressed when Pd is above Ni. Sharp *d*–Ni peak is splitting up to three peaks and center of gravity of Ni bands lie lower in energy in comparison with that of bulk–like layer. The Pd states are shifted downward by about 1 eV in comparison with clean Pd (110) but Pd main peak lies close to EF than Ni one. Shape of Pd surface DOS in Pd/TiNi (110) changes significantly in contrast to clean Pd (110) but total DOS structure near EF changes insubstantial. The main difference of Pd/NiTi (110) surface ES from Pd/FeTi (110) is that states induced by Pd–Ni bond lye essentially deeper relative EF and it may be a reason of comparatively low TiNi adsorption capability.

4 CONCLUSIONS

The hydrogen adsorption on clean *B*2–TiNi (001) and Pd–covered TiNi (001) and (110) surfaces were studied. We found that hydrogen adsorption is preferable on Ti–terminated TiNi (001) surface with H in "hollow" position. We investigated the influence of Pd coating on the surface ES and chemical bond on TiNi (001) and (110) surfaces. It was shown that Pd influences the surface ES significantly when it was placed instead of Ti in TiNi (001). Ni states are more reactive with presence of palladium. Hydrogen adsorption is easier for PdNi/TiNi (001) as earlier was found for PdFe/TiFe (001) system. It was found that in Pd–covered TiNi (110) hydrogen is below Pd layer after relaxation. Since Pd coating is well permeable for hydrogen the adsorption properties of Pd–covered and clean TiNi (110) can be the same. 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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