

Theoretical study of the surface electronic structure and hydrogen adsorption properties in advanced hydrogen storage materials

S.E. Kulkova^{a,*}, V.E. Egorushkin^a, D.I. Bazhanov^b,
S.V. Ereemeev^a, S.S. Kulkov^a

^a *Institute of Strength Physics and Materials Science of the Russian Academy of Sciences, Siberian Branch, Tomsk 634021, Russia*

^b *Moscow State University, Moscow 119992, Russia*

Received 16 July 2004; received in revised form 11 December 2004; accepted 12 January 2005

Abstract

We present ab initio investigation of the surface electronic structure for several Ti- and Pd-based alloys. Hydrogen adsorption on the low-index clean surfaces and with Pd coating is discussed. The adsorption of atomic hydrogen is found to be preferable on the Ti-terminated B2-TiMe(001), where Me = Fe, Ni, Pd and on the Ta-terminated PdTa(001) surface. The Me-bridge geometry is the most stable among four sites considered for adsorption onto TiMe(110) surface.

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PACS: 71.20.Lp; 71.20.Be; 71.20.At

Keywords: Hydrogen storage alloy; Thin films; Electronic band structure

1. Introduction

The development of new structural materials for hydrogen energetics needs the understanding at the microscopic level the nature of physical–mechanical properties and complex processes in the bulk and surface. The feasibility of prediction materials properties, the considerable reduction of the expenditures for experimental investigations using computer techniques attracts great attention of specialists in materials science. Conventional total-energy calculations based on the full-potential all-electron techniques allow one to understand the microscopic origin of different phenomena in the bulk and surface and to be the basis for the “atom-

istic engineering” of materials. Despite numerous experimental investigations of hydrogen accumulation by transition metals and alloys the role of alloying elements in increasing of hydrogen capacity is not well understood [1–5].

The modification of surface electron properties by the H adsorption and the effect of a surface reactivity on hydrogen capacity also remains an open question. No adequate theoretical substantiation has been provided as to the hydrogenation ability of titanium alloys as insufficient captivation of interstices by hydrogen. The explanation of physical–chemical nature of the hydrogen adsorption at the metal alloy surfaces [7,6], prediction of their properties, and possible reaction pathways still remain a challenge.

The aim of this work is the investigation of the electronic structure (ES) and hydrogen adsorption at low-index surfaces in the set of titanium and palladium

* Corresponding author. Tel./fax: +7 3822 492576.
E-mail address: kulkova@ms.tsc.ru (S.E. Kulkova).

based alloys. We also study the influence of Pd coating on the hydrogen adsorption properties in B2-TiFe and TiNi alloys.

2. Method of calculation

The full potential linearized-augmented-plane-wave (FLAPW) method [8] within the local density approximation (LDA) for the exchange-correlation potential is applied for ES calculations of clean low-index B2-TiMe surfaces as well as with hydrogen in the different high-symmetry sites. Using the supercell technique, the surfaces are simulated by repeated 5–9 layers slabs (5 layers for the (110) surface, 7 layers for (100) surface, and 9 ones for (100) surface with palladium coating) separated in one direction by a vacuum region of ~ 10 Å. The electron energy spectrum is calculated at 15 and 24 k -points in the irreducible part of the two dimensional Brillouin zone for (001) and (110) surfaces respectively. The lattice parameters $a = 2.976$, 3.015 , 3.18 Å are used for B2-TiFe, TiNi, TiPd alloys and $a = 3.279$ Å, $b = 6.036$ Å for tetragonal PdTa alloy. The interlayer distances are optimized with a damped Newton dynamics. We find a minimum of the adsorption energy (E_{ad}). For this goal E_{ad} is calculated as a function of the distance between the H atom and the surface layer. The adsorption and binding (E_{b}) energies are calculated in accordance with equations from Ref. [9]. The adsorption energy is $E_{\text{ad}} = -1/N_{\text{H}} \times (E_{\text{H/substr}} - E_{\text{substr}} - N_{\text{H}}/2E_{\text{H}_2})$, where E_{H_2} is energy of hydrogen molecule. The binding energy is $E_{\text{b}} = -1/N_{\text{H}}(E_{\text{H/substr}} - E_{\text{substr}} - N_{\text{H}}E_{\text{H}})$, where E_{H} is energy of hydrogen atom. N_{H} is the number of hydrogen atoms per metal atom in a surface layer.

3. Results and discussion

The idealized B2-TiMe(001) surface can be terminated by either Ti or Me atoms. For one monolayer coverage so-called “hollow” position on the Ti-terminated TiMe(001) is found to be preferable for H adsorption. The equilibrium positions of hydrogen on both Ti- and Me-terminated TiMe(001) surfaces (Ti/TiMe and Me/TiMe), E_{ad} and E_{b} are listed in Table 1. The maximum in the adsorption energy (in accordance with definition, the positive E_{ad} value means preference of H adsorption) in TiFe(001) is observed at practically the same H position as in pure Fe(001) (around the distance of the Fe–H bond length ~ 1.8 Å). These values are 1.74 Å for Fe–H and 1.88 Å for Ti–H in Ti- and Fe-terminated TiFe(001), respectively. The binding energy of hydrogen in 3d transition metals is around 3 eV with a small variation across the series. The preference of the Ti-terminated TiFe(001) surface for hydrogen adsorp-

Table 1

The calculated energies E_{ad} and E_{b} in eV, the height (h_0) on the stable adsorption site above the surface layer in Å

	E_{ad}	E_{b}	h_0
H–Ti/TiFe(001)	0.75 (0.78)	3.12	0.48
H–Fe/TiFe(001)	0.73 (0.97)	3.09	0.76
FM H–Fe/TiFe(001)	0.56 (0.72)	2.94	0.74
H–Ti/TiNi(001)	0.88 (0.81)	3.25	0.46
H–Ni/TiNi(001)	0.67 (0.72)	3.05	0.65
H–Ti/TiPd(001)	0.34	2.72	0.52
H–Pd/TiPd(001)	0.28	2.66	0.52
H–TiFe(110)	0.54	2.92	0.62
H–TiNi(110)	0.14	2.52	0.64
H–TiPd(110)	0.28	2.66	0.92

Values in brackets are for unrelaxed surfaces.

tion is only due to the magnetism of the Fe surface layer ($2.27\mu_{\text{B}}$) [6]. For the ferromagnetic Fe-terminated TiFe(001) surface hydrogen adsorption leads to decrease of magnetic moment of the Fe surface atoms ($1.81\mu_{\text{B}}$). The Ni-terminated TiNi(001) surface is non-magnetic in agreement with experiment. We find that the adsorption energy is very sensitive to the surface relaxation (values in parentheses are given for the bulk-terminated surface). Actually, the relaxation influences the electronic structure only for the first two surface layers. The layer-resolved densities of states (DOSs) of H-covered TiNi and TiPd(001) surfaces in comparison with those of clean films for Ti-terminated surfaces, are shown in Fig. 1.

H–Me bonding states appear below the d-band bottom of the clean TiMe surface. The nature of the surface chemical bond is easily clarified by examining layer-resolved and partial DOSs [6]. The hybridization of hydrogen states with d-bands of Me and Ti is localized in the real space and only the surface and subsurface

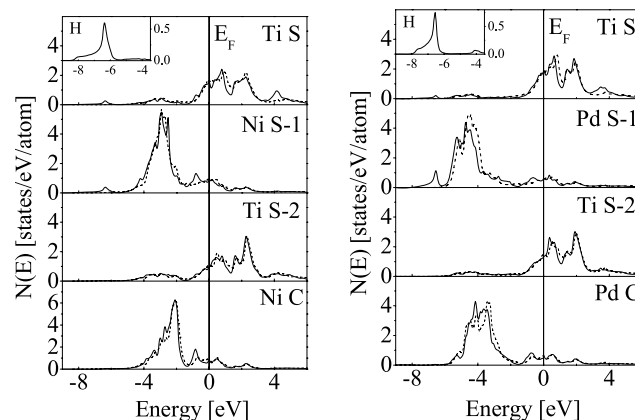


Fig. 1. Layer resolved DOSs of H-covered Ti/TiMe(001) films (solid lines), results for clean surface are shown by dashed lines. The labels C and S denote the central and surface layers, respectively. The labels S-1 (subsurface) and S-2 correspond to the position of layer from the surface.

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