# Adsorption of hydrogen atom on intermetallic aluminide surface

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Favorable adsorption sites for a hydrogen atom on transition metal aluminide surfaces are investigated by *ab initio* Hartree-Fock calculations. On a TiAl surface, two chemisorption sites, i.e., a fourfold-coordinated hollow site and a Ti-atop site, exist. An adsorption path analysis of a hydrogen atom suggests that the hydrogen atom adsorbs a metastable Ti-atop site first and then about 0.2 eV is needed to displace that from a Ti-atop site to the most stable hollow site. It is possible to distinguish between the two hydrogen positions since the electronic structures of these surface systems are quite different.

We also investigate Al(100) surfaces adsorbed by a hydrogen atom on the same chemisorption sites as those of TiAl(100) surface and discuss the origin of the difference between the electronic properties of the two surfaces.

## 1. INTRODUCTION

Transition metal aluminides are of great concern because of their useful applications. Among those aluminides, TiAl is one of the typical transition metal aluminide. The crystal structure of TiAl is the fcc-type $L1_0$ structure and is composed of Ti, a 3d transition metal which is characterized as its narrow 3d band, and Al, a nearly-free-electron metal. It has been mostly applied toward structural material until now because of its extraordinary hardiness and high melting temperature. At present, a theoretical and experimental investigations of adsorption on a TiAl surface have also been carried out [1-4] extensively to elucidate an adsorption process and surface chemistry since TiAl provides a prototype of a bimetallic alloy surface, though usual investigations are handling with polycrystalline substrate of TiAl.

In this paper, an adsorption sites on a TiAl surface has been examined, using a hydrogen atom as an adsorbate. First, we present a potential energy map of a hydrogen atom on a TiAl surface and discuss its favorable adsorption sites. Next the electronic density of states are calculated in order to understand the electronic properties of hydrogen-adsorbed TiAl surfaces. This paper is organized as follows. In the next section, a model of a TiAl surface is introduced and the method of calculations is described. In the section 3, numerical results of the electronic properties of the surfaces are presented. A summary is given in the last section.

## 2. MODEL AND CALCULATION

The crystal structure of TiAl is a fcc-type $L1_0$ structure, in which Ti and Al layers stack alternatively toward the (001) direction. Although TiAl substrate used for usual experiments are polycrystalline, we have investigated (100) surface of single crystal TiAl in the present study in which the same number of Ti and Al atoms appear. We consider a three-layer TiAl(100) slab chemisorbed by a hydrogen atom on both sides of the slab with the coverage of $\theta = 0.5$. A hydrogen chemisorbs either on a hollow site or an atop site. We calculates total energies of hydrogen-chemisorbed surfaces varying adatom heights using the Hartree-Fock program CRYSTAL88 [5] and find the stable height for a hydrogen atom on an each sites. Then we compare hydrogen-chemisorbed TiAl and Al surfaces by calculating total and partial density of states (DOS) spectra and energy band structures. The basis sets adopted in the present calculations are referred from Huzinaga's [6]. The exponents and coefficients of the inner shell orbitals used here are the same as the Huzinaga's, but those of the valence shell orbitals, especially delocalized GTOs (Gaussian-type orbitals), are altered following the modification procedure as proposed in Ref.5 so as to avoid charge oscillations and achieve well energy convergence.
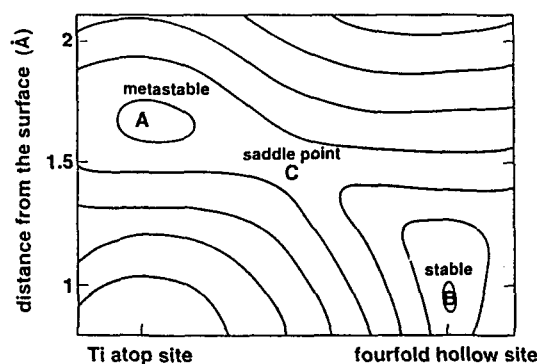
Fig. 1. A potential energy map of a hydrogen atom as a function of its height above the TiAl(100) surface.

# 3. NUMERICAL RESULTS

## 3.1. Site preference

The most favorable adsorption site for a hydrogen atom on TiAl(100) surface is found to be a fourfold-coordinated hollow site, and then a Ti-atop site comes next. The adsorption energy is 4.0eV for a stable hollow site and 3.4 eV for a metastable Ti-atop site. There is a saddle point whose energy is 0.2eV less favorable than the metastable Ti-atop site in the middle of the two sites. The adatom heights at a hollow site, a Ti-atop site and a saddle point site are 1.0Å, 1.7Å and 1.4Å, respectively. Figure 1 shows a schematic potential energy map of a hydrogen adatom on the TiAl(100) surface as a function of its height above the surface. According to the potential energy map, it is found that a hydrogen atom approaching to the surface chemisorbs on a Ti-atop site because there is no barrier in the adsorption process though this site is not energetically the most favorable site. To displace the hydrogen atom from the metastable Ti-atop site toward the most stable hollow site, the activation energy of 0.2eV is required. Even if the hydrogen atom is trapped in the metastable Ti-atop site according to the chemisorption path stated above, it is expected that hydrogen atoms exist on either sites in a thermal equilibrium.
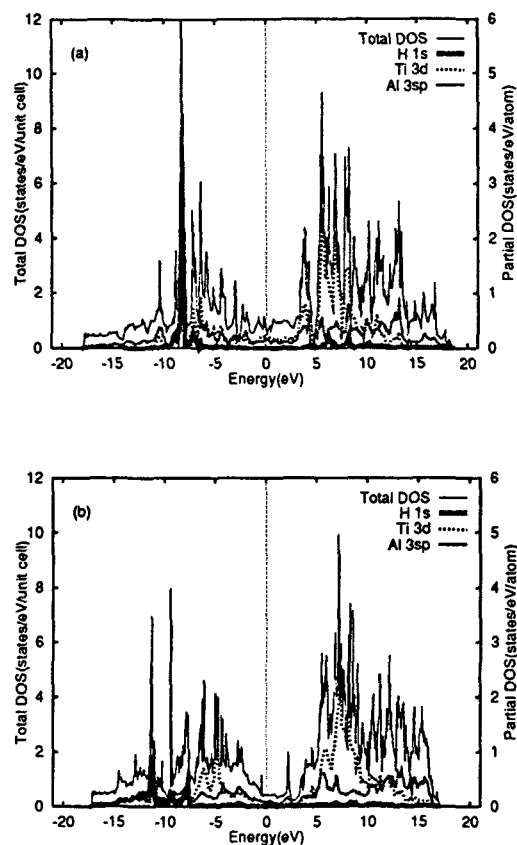
Fig. 2. Calculated total and partial density of states of TiAl(100) surface.

(a) A hydrogen atom adsorbs on a Ti-atop site on the TiAl(100) surface.

(b) A hydrogen atom adsorbs on a hollow site on the TiAl(100) surface.

We have also calculated Al(100) surfaces chemisorbed by a hydrogen atom on the same adsorption sites as those of the TiAl(100) surface for comparison, though the most stable adsorption site for a hydrogen atom on an Al(100) surface is known as a bridge site. Adsorption energies for a hollow and Al-atop sites as a function of adatom height are found to be 1.3eV (1.1Å above the surface) and 2.3eV (1.6Å above), respectively. Adatom heights show a good agreement with those obtained by density functional calculation on the Al(100) surface [7]. The adsorption energies for a hydrogen atom on a hollow and Al-atop sites of the Al(100) surface are both small in comparison with those of the

864

Table 1. Mulliken charge for valence shells of the surface atoms of TiAl and Al. Al-1 and Al-2 indicate nonequivalent atoms in the case of $\theta = 0.5$.

| | TiAl clean surface | H/TiAl Ti-atop site | H/TiAl hollow site |
|---|---|---|---|
| H $(1s^1)$ | —— | 1.442 | 1.587 |
| Ti $(4s^23d^2)$ | 3.535 | 3.405 | 3.360 |
| Al $(3s^23p^1)$ | 3.108 | 2.849 | 2.904 |

| | Al clean surface | H/Al Al-atop site | H/Al hollow site |
|---|---|---|---|
| H $(1s^1)$ | —— | 1.391 | 1.499 |
| Al-1 $(3s^23p^1)$ | 2.960 | 2.714 | 2.731 |
| Al-2 $(3s^23p^1)$ | 2.960 | 2.906 | 2.731 |

TiAl(100) surface. In addition, an adsorption for the hollow site is less favorable than that for the atop site at Al(100) surface, which is the opposite to the case of TiAl(100) surface.

### 3.2. Electronic structure

Next the electronic states of the hydrogen-chemisorbed TiAl(100) surfaces are discussed. In Fig.2, we show the total and partial density of states (DOS) of the TiAl(100) surfaces for a hydrogen atom adsorbed on (a) a Ti-atop site and (b) a hollow site. One can find a significant difference in the electronic states between the two surfaces for a hydrogen atom adsorbed on a hollow and a Ti-atop sites. When a hydrogen atom chemisorbs on a Ti-atop site, H1s state interacts strongly with Ti3d state and causes bonding-antibonding splitting, which can be notified from the Fig.2(a) where the sharp peak at the energy level of -8eV shows the bonding state. On the contrary, a hydrogen adsorption phenomenon on a hollow site of the TiAl(100) surface does not affect characteristic change in electronic states (Fig.2(b)).

In the case of the hydrogen-adsorbed Al(100) surfaces, a hydrogen adsorption merely shifts the energy level towards the lower energy side and the electronic structure is not changed essentially by a hydrogen adsorption process. Thus a change in the electronic structures of surfaces can be explained simply from the rigid band model.

### 3.3 Charge transfer

Numerical results of Mulliken's population analysis are collected in Table 1. In spite of the fact that the Pauling electronegativity of Ti and Al are

both 1.5, there is a large electron transfer from a Ti atom to an Al atom on a clean surface of TiAl(100). In the case of an adsorption of a hydrogen atom of which the electronegativity is 2.1, the adsorption causes a larger electron transfer from a Ti atom to a hydrogen adatom than that from an Al atom, and, consequently, a total amount of charge transfer from a TiAl substrate to a hydrogen adatom is larger than that from an Al substrate. A large charge transfer on a hydrogen-chemisorbed TiAl surface increase total energy of the surface system because of a large direct Coulomb interaction energy. A rough estimation of the Coulomb energy between a substrate and a hydrogen atom on the hollow site is about 2eV greater than the energy between an Al substrate and a hydrogen atom on the hollow site, where the energy difference calculated by *ab initio* Hartree-Fock method is 2.7eV. Thus the large adsorption energy on a TiAl surface can be understood from a tendency of a large charge transfer on the TiAl surface.

### 4. SUMMARY

In this paper, we have presented the results of the adsorption of a hydrogen atom on the TiAl(100) surface, which is a prototype of bimetallic surface. We first calculated a total energy of hydrogen-adsorbed three-layer TiAl(100) slab by *ab initio* Hartree-Fock calculations and drew a potential energy map of a hydrogen atom on the surface. We found that the most stable adsorption site for a hydrogen atom is a hollow site, and the next one is a Ti-atop site where there is an energy barrier between

the two sites. Though energetically the most favorable site is a hollow site, a hydrogen atom adsorbs on a metastable Ti-atop site because there is no energy barrier in the approaching path from a vacuum region to a Ti-atop site. In the viewpoint of the electronic states, a hydrogen adsorption to a metastable Ti-atop site and a stable hollow site differs completely each other. The former electronic state shows strong binding between H1s states and Ti3d states, meanwhile the latter indicates the coupling between H1s states and Al3sp states rather than Ti3d states. We have also presented the result that there is a large amount of charge transfer from TiAl substrate to a hydrogen adatom, where a Ti atom plays an essential role in charge transfer though the electronegativities of Ti and Al are the same. Since the surface electronic state substantially changes according to the hydrogen-chemisorbed site, a controlling of surface electronic properties by a hydrogen chemisorption process will be possible in the future.

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