

Formation of cobalt hydrides in low temperature field evaporation

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In the field evaporation process of cobalt in an atmosphere of hydrogen 10^{-6} Pa at a temperature of 20 K, both the ions of cobalt and the ones of CoH_x (where $x = 1, 2$ and 3) have been observed. Since cobalt hydride is typically produced in the direct reaction of cobalt with hydrogen under a pressure of 5 GPa at 600 K, the result of this experiment, which has been carried out under so different conditions, points to the possibility to apply quite a different method of obtaining hydrides of transition metals. The possibility to synthesize such compounds on the surface of cobalt in the high electric field is analysed thanks to quantum chemical methods of calculation (the density functional theory – DFT). Calculated is the equilibrium geometry, the binding energy, and the ionization potential of the cobalt-hydrogen complexes recorded in the experiment. Basing on the computed values and on the measurement of the desorption ions energy distribution, the bond energy of the complexes with the surface has been calculated. Also, the activation energy of filling tetrahedral and octahedral interstices by hydrogen has been determined. Concluding assertion is that the high electric field present at the surface of cobalt during the field desorption process may be the crucial agent that is responsible for the formation of cobalt hydride at the surface.

Keywords: cobalt hydrides, field evaporation, *ab initio* calculations.

1. Introduction

Hydrogen absorption and adsorption properties of intermetallic compounds are extensively investigated as the potential candidate for fuel storage for energy consumption applications and as prospective materials for neutron radiation shielding. Many metals and alloys may react spontaneously with hydrogen. These materials, either defined compounds or solid solutions, are designed as metallic hydrides [1]. It is important to emphasize that only the techniques of compressing gaseous hydrogen to pressures of a few gigapascals have made it possible to synthesize hydrides of most transition metals, such as cobalt hydrides [2]. Then, metal hydrides are of extreme interest for high pressure chemistry.

This work was undertaken in an attempt to elucidate quite a different reaction mechanism between hydrogen and cobalt surface. The reaction proceeds in the presence of the high electric field. Electrostatic field of the strength of several volts

per nanometer, used in the field emission desorption process [3], is of the same order of magnitude as the intrinsic fields of an atom or molecule. Therefore, it is not surprising that such a field influences considerably atomic or molecular orbitals, which in turn leads to phenomena described by a new speciality called field induced chemistry [4]. One of the most important phenomena of interest is the synthesis of metal-hydrogen complexes by means of low-temperature field-evaporation of a metal in the presence of the hydrogen gas phase [5]. For example, complexes like CoH_x^+ ($x = 1, 2, 3$) created during field evaporation of cobalt are of special importance.

2. Experimental and calculations

The instrument [6] used in this investigation was a high-resolution pulsed-laser time-of-flight atom-probe (PLTFAP) field ion microscope. The ultrahigh vacuum experimental conditions and the measurement procedure were those described in [5]. The field emitter tip was obtained by means of electropolishing of cobalt wire of 99.99% purity. The cobalt tip was kept at a temperature of 20 K. The applied electric field strength was 31.3 V/nm. The partial pressure of hydrogen was 10^{-6} Pa. Before each experiment, the emitter surface was processed to obtain an atomically smooth end-form by low-temperature field evaporation in the presence of neon. The emission occurred from (0001) Co steps.

The quantum chemical calculations have been performed in order to interpret the results. For numerical computations, the GAUSSIAN 98 program package [7] was employed. The density functional theory (DFT) was applied to calculate the energy of the hydrogen-cobalt complex using a hybrid functional (B3LYP). The basis set taken for cobalt atom was 6-31G.

3. Results and discussion

During the process of field desorption of cobalt in the atmosphere of hydrogen the ions H^+ , H_2^+ , and H_3^+ were detected [8], as well as cobalt ions and cobalt-hydrogen ions CoH_x^+ ($x = 1, 2, 3$) [9]. The obtained mass spectrum is shown in Fig. 1.

In the present investigation the energy distributions were also measured using the time-of-flight method [10] and basing on them, the field ion appearance energy has been determined. Energy distributions of all ions show a very narrow distribution width. The shape of the curve proves that the detected ions are formed in the strictly specified place, just outside the metal surface [11]. The appearance energy of n -fold charged field-desorbed ions can be expressed from a thermionic cycle by [12]

$$A_n^{hkl} = \sum_{i=1}^n I_i + A^{hkl}(F) - Q(F)$$

where I_i is the i -th ionization energy of an atom, $A^{hkl}(F)$ is the binding energy of the atom (or the adsorption energy) in the high electric field at the (hkl) plane of the tip

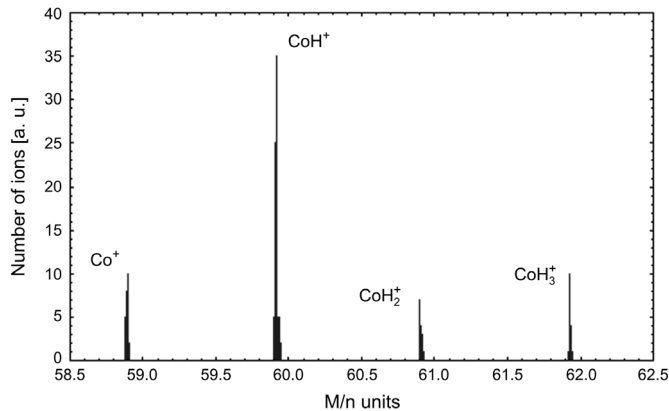


Fig. 1. Pulsed-laser field evaporation mass spectrum of cobalt and cobalt hydride ions.

surface and $Q(F)$ is the activation energy for field evaporation of the atom. Neglecting temperature effects (in our case $T = 20$ K) and a relatively small activation energy, the binding energy can be calculated from the Equation. Also in the case of cobalt-hydrogen complex the binding energy can be evaluated basing on these relations, where the respective values of the ionization potential and other quantities for a cobalt-hydrogen molecule should be put in the Equation instead of such data for cobalt. These quantities, however, cannot be determined by means of the experiment. We have calculated the total binding energy E_b and ionization potential I_n of the cobalt-hydrogen molecule using a quantum chemistry method. The geometry of a molecule in the equilibrium state was calculated by minimization of the total energy with respect to all its independent inner coordinates, *i.e.*, the bond length, valence angles and dihedral angles. In Table 1 results of these calculations are collected. Putting calculated values into the Equation, we were able to predict the value of the adsorption energy of the measurement species, which is also shown in Tab. 1. In addition, the values of bond

Table 1. Binding characteristics of cobalt hydrides in the equilibrium states.

Species	Binding energy of H atom [eV]	Ionization potential I_1 [eV]	Adsorption energy A^{hkl} [eV]
CoH	2.21	7.04	1.71
CoH ₂	3.06	8.93	2.76
CoH ₃	2.74	6.88	2.36

Table 2. Geometry of cobalt hydrides.

Molecule	Co-H distance [nm]	H-Co-H angle [deg]
CoH	0.144	—
CoH ₂	0.151	121.4
CoH ₃	0.147	102.5

lengths and valence angles of considered molecules in the equilibrium state are summarized in Tab. 2. On the basis of these data and also calculations in an external electric field we can state that the CoH_x molecules are stable as long as the field strength is not higher than 32–35 V/nm and CoH_x^+ is stable up to 35–40 V/nm. The calculated binding energies between Co–H are comparable to the measured energy in the chemisorption process on the Co(0001) plane [13–15], as well as to other theoretical calculations on the *fcc* hollow sites and *hcp* hollow sites [16].

The chemisorption stage is a precursor for a progressive chemical attack of the hydrogen atoms also on the bulk metal, leading to the occupation of the so-called subsurface site, to the bulk diffusion and, finally, to hydride compound formation. In the *hcp* structure, there are two types of highly symmetrical interstitial sites conforming

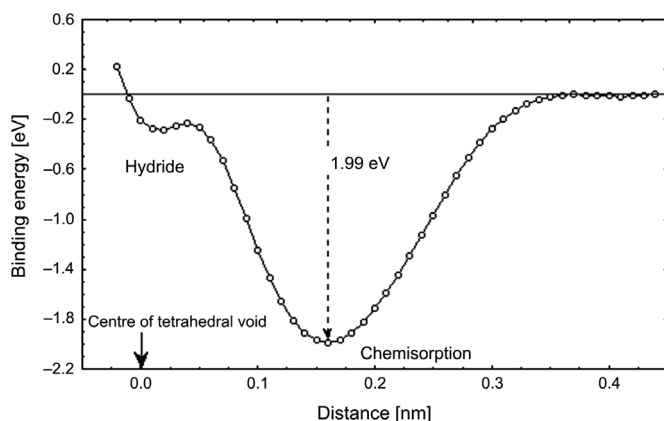


Fig. 2. Calculated binding energy changes as dependent on the distance between hydrogen atom and four-atom cobalt cluster.

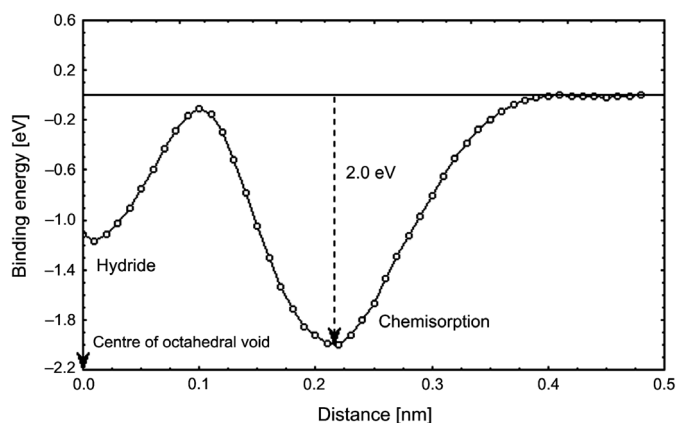


Fig. 3. Calculated binding energy changes as dependent on the distance between hydrogen atom and six-atom cobalt cluster.

to the $P6_3/mmc$ space group, the octahedral and tetrahedral position. The crystal symmetry of metal hydrides is usually the same as that of pure metals because hydrogen atoms randomly occupy the interstitial sites. In the case of cobalt hydride, however, the crystal symmetry is changed due to the hydrogen ordering. Neutron diffraction studies on $\text{CoD}_{0.5}$ [2] have revealed that hydrogen occupies every second octahedral interstices along c -axis of an hcp lattice, which results in an anti- CdI_2 structure. It is important to emphasize that the authors not only did not find any superstructure, but also any significant changes of the lattice parameter in the case of CoH . As the next step towards the understanding of the interaction between hydrogen and cobalt surface we have made calculations for the system of a hydrogen atom and a four- (like the tetrahedral void) and a six-atom (like the octahedral void) cobalt cluster. Diagram of the binding energy as a function of the distance is shown in Figs. 2 and 3.

As can be seen in these figures, the binding energy of hydrogen in the threefold hollow is the same in both cases and is equal to about 2.0 eV. The results of this calculation are in certain divergence with the experimental value 2.6 eV [13]. It can be probably due to a small number of cobalt atoms taken into account. Hydrogen produces the ordered chemisorbed H-phases without reconstruction of the $\text{Co}(0001)$ surface. To diffuse into a tetrahedral or an octahedral void and to create hydride, a hydrogen atom should pass over the barrier of activation energy of 1.76 and 1.89 eV, respectively. The binding energy of hydrogen with the tetrahedral void is 0.29 eV instead, and with the octahedral void it is 1.17 eV. Due to the applied electric field, the field-free atomic interaction curve becomes bent down and shifted towards the low total energies. This indicates the occurrence of an effect in which the binding energy of the H-Co complex reveals an increase and the activation energy diminishes or disappears. According to this model, the activation energies for the inverse process are 0.06 and 1.06 eV, respectively, and after the withdrawal of the applied electric field, the hydrogen may remain in the surface monolayer of cobalt, but only in the case of filling the octahedral voids. This interpretation is also consistent with earlier experimental results [2].

In view of the results presented, we believe that cobalt hydride interstitial compound is formed in the high electric field in the sites within two topmost monolayers (of the $(0001)\text{Co}$ plane) and that during the low-temperature field evaporation process it is desorbed and detected as CoH_x molecules.

Acknowledgements – The experimental part of this work was done in the laboratory of prof. Tien T. Tsong at the Institute of Physics, Academia Sinica, Taipei, Taiwan, ROC. The author expresses gratitude to Professor Tsong for hospitality and fruitful discussions during the course of the visit.

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Received June 6, 2005