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in the presence of PT

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Reactivity of Hydrogen with Uranium in the presence of Pt

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ABSTRACT

The surface-reaction of di-hydrogen with uranium in the presence of Pt clusters has been studied using scanning tunneling microscopy (STM). Uranium was deposited on highly oriented pyrolytic graphite (HOPG) and annealed at temperatures up to 1200 °C to obtain atomically flat surfaces. Pt clusters were then formed using evaporation from a Pt source onto the surface and subsequent annealing. Hydrogen mainly attacked uranium in the vicinity of Pt clusters and formed hydride. The hydride formation probability for the most probable cluster size has been determined. This probability is almost constant at 2.3x10^-4 over the range of exposures studied.

1.0 INTRODUCTION

Recently, the interactions of hydrogen and water with pure and slightly oxidized uranium have been studied. The sticking probability and binding energies were deduced from temperature programmed desorption (TPD), and the hydride formation and recombination probabilities were determined by modulated molecular beam techniques [1]. In addition, using atomic force microscopy, it was shown that exposure of a slightly oxidized surface of uranium to di-hydrogen leads to raised features mainly along the grain boundaries. The features were postulated to be regions where hydriding had been initiated, since the uranium to uranium hydride transformation involves a volume increase of a factor of 1.8. These features continued to grow in size with exposure, while the density of features did not change noticeably.

The present investigation was designed to determine whether a metal with high sticking and dissociation probabilities for di-hydrogen deposited on the uranium surface could serve as a source of H atoms and thus lead to a local enhancement of hydriding. A similar idea was implemented before to accelerate the gasification of carbon using Pt as a catalyst to dissociate hydrogen [2]. The resulting site specific hydriding is monitored in situ by STM. The mechanism for hydride formation is dissociation of hydrogen on Pt, diffusion of adsorbed hydrogen toward U/Pt interface sites, recombination and desorption as di-hydrogen or formation of hydride at those sites.

2.0 EXPERIMENTAL

To investigate the initial hydriding using STM with nanometer-scale resolution, it is essential to start with a high purity, atomically flat uranium substrate. This cannot be achieved by polishing since an uranium surface oxidizes extremely rapidly in a laboratory atmosphere and consequently electron tunneling cannot be established under the STM tip. This difficulty has been overcome here by laser ablation of an uranium target and consequent deposition of the ablated uranium onto highly oriented pyrolytic graphite in a UHV system with a base pressure of 6x10^-9 Pa. HOPG with an atomically flat surface acts...
as an ideal substrate. Platinum was deposited by evaporation. The sample was then annealed to create clusters with different sizes.

The heart of this experiment was measurement using the high spatial resolution of an STM[4]. The STM used for these experiments contained a cylindrical Piezo crystal which facilitated x, y, and z motion of the tip. The range of motion for this STM was 1.4 µm in x and y and 0.4 µm in z. Constant-current-mode images were used with the bias voltage usually set to 500 mV (sample positive), and the tunneling current was set at 0.6 nA.

3.0 RESULTS

The results of 5 min. and 20 min. exposures to di-hydrogen on samples with Pt clusters are shown in figures 1a and 1b. It appears that the clusters expand as the result of hydrogen exposure. The apparent expansion is due to reaction of hydrogen with uranium in the vicinity of the perimeter of clusters. Since there is an increase in volume due to the conversion of uranium to its hydride it is reasonable to assume that hydride rings are being created and expand around the clusters. By scanning over the area many times, the clusters disappear and are replaced by pits as disks with depth of 5.5 Å. Since hydride forms as powder it can easily be swept away by the STM tip and thus only the unreacted uranium is imaged after many cycles of scanning the area.

The radial expansion, $R(t)$, of hydride around a Pt cluster as a function of time normalized to the radius of the Pt cluster ($R(t)/r_P$) is measured. The expansion is nonlinear with time. To obtain the catalytic strength of Pt to convert U to its hydride, we define the hydriding probability as the ratio of the hydrogen uptake to form hydride in the vicinity of the most probable Pt cluster size to twice the number of di-hydrogens striking at the cluster during the exposure. From the size of the pit, assuming β structure of uranium, the number of uranium atoms swept away during multiple scans can be calculated. The hydrogen uptake is three times this number. The number of di-hydrogens striking at the cluster during the exposure can also be easily calculated by the kinetic theory of gases. The hydriding probability ($\varepsilon$) can be expressed as:

$$\varepsilon = 0.277 \frac{\left( \frac{R}{r_P} \right)^2 - 1}{t}$$

were $t$ is seconds and $R$ is the measured hydride radius. This probability appears to be independent of time at high exposures. It appears, however, it is decreasing with time at short exposure. Unfortunately, shorter exposures could not be accurately achieved because the hydrogen leak-valve had to be opened and closed by hand, and because hydrogen pumps out slowly.
4.0 DISCUSSION

The sticking probability of di-hydrogen on platinum has been determined previously. Christmann and Ertl determined initial sticking probability values of .35 and .08 for Pt(997) and Pt(111) surfaces respectively. The values decreased with coverage [3]. Shen reported a value of .5 at coverage of about .1 for Pt(110) which reduced with coverage as well [4]. The sticking probability of di-hydrogen on the clusters is estimated to be between $5 \times 10^{-2}$ to $1 \times 10^{-1}$, much higher than on well-ordered uranium. Pt acts as a catalyst to dissociate di-hydrogen and thus provides adsorbed atomic hydrogen to the surrounding uranium. Hydride formation starts at the Pt-Uranium boundary and expands from then on at the uranium step generated. The existence of flat-bottom pits and the fact that no attack occurs on uranium terraces suggest that the hydride formation probability on an ordered uranium surface is low compared to that on steps or defects.

REFERENCES


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100 nm

Figure 1. STM images of Pt catalyzed uranium hydriding as exposed to hydrogen at $1.3 \times 10^{3}$ Pa. a) after 5 min. and b) after 20 min. exposures.