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Adsorption of hydrogen on clean and modified magnesium films

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The sticking of hydrogen on 400 Å thick magnesium films, grown under ultrahigh vacuum conditions, have been measured under conditions relevant for hydrogen storage, i.e., elevated temperatures and pressures. A model which describes the hydrogenation and desorption kinetics of the pure magnesium films at H/Mg ratios less than 2% is developed. The activation barrier for hydrogen dissociation is 72 ± 15 kJ/mole H_2, and a stagnant hydrogen uptake is observed. For platinum-catalyzed films, the barrier is significantly reduced, and there is no stagnation in the uptake rate.

The interaction of hydrogen with metals has always attracted much attention due to its fundamental relevance for a number of industrially important processes. Furthermore, hydrogen is the simplest molecule and has therefore been used as a model system for understanding the basic principles of solid-gas interaction. Most of the work concerns dissociative adsorption of hydrogen on transition metals and has been motivated by its relevance for catalysis. The contributions are both theoretical[1–7] and experimental[8–11] and references therein. Recently, materials for hydrogen storage have obtained renewed interest and the initial sticking of hydrogen on nontransition metals is of particular interest.[12] One of the systems, namely magnesium, has obtained special attention, being a model system for hydrogen storage applications.[13] However, the vast majority of the investigations are studies of ball-milled powders which prevents detailed surface-sensitive characterization.

The only available ultrahigh vacuum (UHV) study on pure magnesium was performed by Sprunger and Plummer,[14] who detailed the interaction of atomic hydrogen with a Mg(0001) single crystal. However, the sticking probability for molecular hydrogen is too low to be studied under UHV conditions, and thermal desorption experiments could not be performed, since that would lead to sublimation of the crystal. Due to these difficulties, accurate quantification of the hydrogen uptake was not possible. Krozer and Kasemo,[15] on the other hand, used a palladium overlayer as a dissociation catalyst in their study of the hydrogen uptake of magnesium films under well-controlled conditions. Here, the hydrogen content was measured by monitoring the mass change of the film, rather than by thermal desorption.

Dissociative adsorption is a crucial step for hydrogen uptake in Mg. In the experiments presented here, we study hydrogenation of magnesium thin films with the help of a combined UHV/high pressure setup. The dissociative sticking of hydrogen on the magnesium films, both with and without a dissociation catalyst, is studied using the high pressure cell, while desorption of hydrogen and magnesium is studied in the UHV chamber. By combining these measurements with modeling, the energy diagram for the interaction of hydrogen with magnesium can be extracted.

The ultrahigh vacuum chamber has a base pressure below 1×10^{-10} mbar and is equipped for ion scattering spectros-

copy, (ISS), x-ray photoelectron spectroscopy (XPS), and thermally programmed desorption (TPD).[16] It also contains a high pressure cell, which allows for hydrogen exposures at pressures up to 4 bar, while preserving the vacuum in the analysis chamber. The substrate used was a Mo(111) single crystal, which was cleaned by cycles of sputtering, followed by annealing at 1073 K. The temperature of the crystal was measured with a chromel-alumel (type K) thermocouple, (thread diameter 0.125 mm), which was spot welded to the edge of the crystal. Magnesium films were evaporated onto the Mo(111) at rates between 0.1 and 0.4 Å/s, as monitored by a commercial quartz crystal microbalance (QCM). Evaporation was performed at a sample temperature of 423 K. In this way, thermal annealing effects during the adsorption experiment could be completely eliminated. At temperatures above 423 K, Mg starts to evaporate from the film. Platinum overlayers were evaporated with the sample at room temperature. The evaporation source was a 99.99% Pt wire, wrapped tightly around a 0.25 mm W wire, yielding evaporation rates around 0.1 Å/min.

In order to avoid contamination of the Mg surface, the hydrogen gas (N57, purity 99,9997%) was cleaned by a reduced Cu catalyst and a molecular sieve. In addition, the high pressure cell was baked in a flow of hydrogen for 15–24 hours, prior to performing experiments. The hydrogen uptake experiments were carried out by admitting hydrogen to the high pressure cell to the desired pressure and then heating the sample to the desired temperature. After high pressure experiments, the Mg films were checked for impurities, such as oxygen, with XPS. The hydrogen uptake was obtained from thermal desorption experiments. The area under the TPD curve for the 2 AMU signal was calibrated with the area obtained from the Mo(111) surface saturated with hydrogen.[16] Hydrogen coverages are reported with respect to the Mg(0001) surface, which has an atomic density of 1.94×10^{19} m^{-2}.

Figure 1 shows the results of uptake experiments on 400 Å Mg films at a hydrogen pressure of 4 bar. It is clear that there is a decrease in the uptake rate with time. The longest exposure time used at 433 K is 5 minutes, since subsequent thermal desorption measurements indicated that significant evaporation of Mg occurred for longer exposure times. Typical desorption curves for Mg and H_2 are shown in
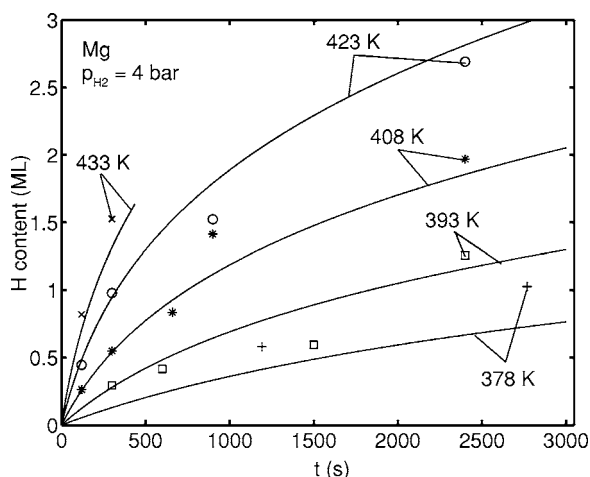
FIG. 1. Hydrogen uptake for 400 Å Mg films with a hydrogen pressure of 4 bar. The curves are calculated from the model with the parameters shown in Fig. 4.

Fig. 2. The desorption of Mg from the Mo(111) substrate has been shown to be independent of the H content in the concentration range investigated here.[16] No evidence of desorption of molecular hydride, MgH$_2$, was found.

In order to investigate the influence of the surface processes on the uptake rate, 0.5 Å Pt, as determined by the QCM, was deposited on top of 400 Å Mg films as a hydrogen dissociation catalyst. The Pt overlayer was characterized with ISS and XPS at room temperature. ISS, which probes the outermost atomic layer, did not show any Pt, while XPS showed the presence of Pt within the probing depth of the Pt 4f line. This strongly suggests alloying or segregation of Mg, even at room temperature. The actual surface coverage of Pt is thus below the detection limit for ISS. Figure 3 shows the results of adsorption experiments on Pt/Mg films at a hydrogen pressure of 1 bar. Two distinct differences are
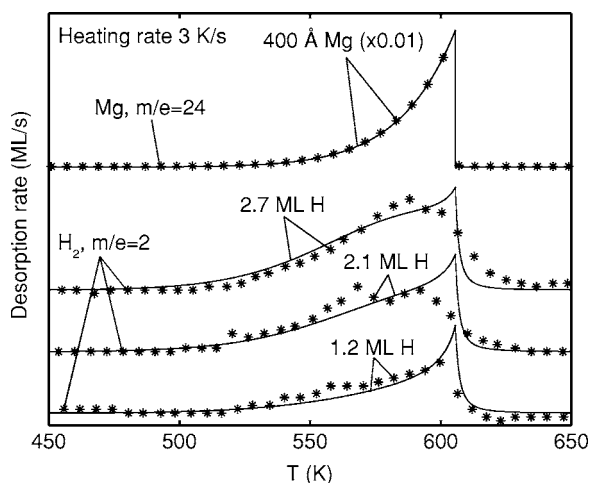

FIG. 2. Hydrogen and Mg desorption curves for 400 Å Mg films loaded with various amounts of H. The heating rate was 3 K/s. The small peaks at 520 and 570 K in the curve for 2.1 ML are random fluctuations. The solid curves are calculated from the model with the parameters shown in Fig. 4.
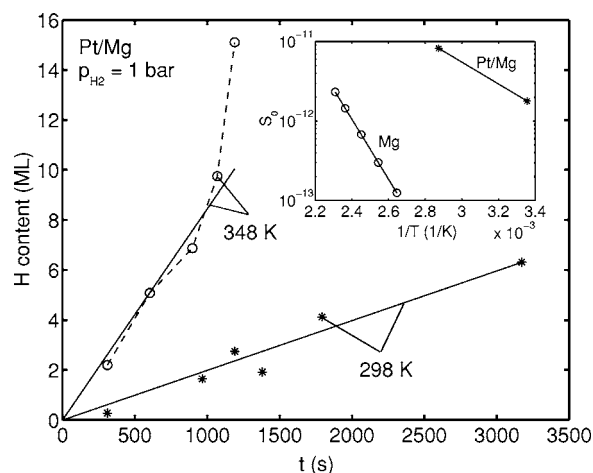

FIG. 3. Hydrogen uptake for 400 Å Mg films activated with 0.5 Å Pt. The hydrogen pressure is 1 bar. The lines are linear fits to uptake data and the inset shows the resulting initial sticking coefficients, S_0. The inset also shows S_0 for pure Mg calculated from Eq. (2).

obvious, compared to Fig. 1. First, the amount of hydrogen sorbed is much higher, despite the lower temperature and pressure used, and second, at least at the lower temperature, the uptake rate is constant. The initial sticking probabilities (sticking coefficients), S_0, were determined from a linear fit to the data points, as shown in Fig. 3. An Arrhenius plot based on the two data points available give a barrier of 26 kJ/mole H$_2$, and a prefactor of 7.3×10^{-8}. The value obtained for the barrier is close to experimental and theoretical values for the bulk diffusion barrier in the α phase, 24 and 18 kJ/mole H, respectively.[17,18] Hence, it is possible that bulk diffusion, rather than dissociation of H$_2$, is the rate determining step for the uptake on Pt/Mg. The small prefactor is probably an effect of the low Pt coverage.

A simple model was developed in order to understand the hydrogen uptake and the TPD experiments on pure Mg films on Mo(111). The model describes the H coverage on the surface and in the bulk. Since Mg desorbs simultaneously with H$_2$, the model also includes the number of Mg layers. Desorption of H$_2$ and Mg is assumed to occur independently from the surface. Since addition of Pt to the Mg surface increases the uptake rate, bulk diffusion is assumed to be fast compared to the processes on the surface. In the model, the H concentration in the bulk is thus assumed to be homogeneous. Since modification of the surface with Pt eliminates the saturation in the uptake curves, it is likely that the saturation is due to blocking of the surface by adsorbed H. Such a situation will arise if the adsorption state of H on the surface is lower in energy than the absorption state in the Mg bulk, as is predicted by calculations.[17,19] The formation of a surface hydride has also been observed experimentally.[14]

The coverage of hydrogen on the surface of the Mg film is denoted by θ_s, the concentration of hydrogen in a bulk layer of the film by θ_b and the number of monolayers of Mg by n_l. The time derivatives of θ_s, θ_b, and n_l are given by the equations

$$\frac{d\theta_s}{dt} = \frac{2S_0(1-\theta_s)^2 F_{H_2}}{N_s} - 2k_d\theta_s^2 + k_{bs}\frac{N_b}{N_s}\theta_b(1-\theta_s)$$
$$- k_{sb}\theta_s(1-\theta_b),$$

$$\frac{d\theta_b}{dt} = \frac{1}{n_l}\left(k_{sb}\frac{N_s}{N_b}\theta_s(1-\theta_b) - k_{bs}\theta_b(1-\theta_s) - \theta_b\frac{dn_l}{dt}\right),$$

$$\frac{dn_l}{dt} = \frac{-F_{Mg}}{N_s}, \qquad (1)$$

where F_{H_2} is the molecular flux of hydrogen. N_s is the surface concentration of adsorption sites [one per surface Mg atom on Mg(0001)], $N_s = 1.94 \times 10^{19}$ m^{-2}, and N_b the number of absorption sites per bulk layer, $N_b = 2N_s$.

The sticking coefficient for H_2 on Mg, S_0, is given by

$$S_0 = S_0^0 \exp\left(-\frac{E_a}{kT}\right), \qquad (2)$$

where S_0^0 is a constant, E_a the activation energy for adsorption, k the Boltzmann constant, and T the absolute temperature.

The desorption of Mg is described by the third of Eq. (1), where F_{Mg} is the molecular flux of Mg,

$$F_{Mg} = \begin{cases} \dfrac{p_{Mg,eq}}{\sqrt{2\pi m_{Mg}kT}}, & n_l > 2, \\ 0, & n_l \leq 2. \end{cases} \qquad (3)$$

Here m_{Mg} is the atomic mass of Mg and $p_{Mg,eq}$ is the equilibrium pressure of Mg (Pa), given by[20]

$$\ln p_{Mg,eq} = 5.006 + 8.489 - 7813/T - 0.8253 \ln T. \qquad (4)$$

The Mg flux is equal to zero for $n_l \leq 2$, since studies on thin Mg films on Mo(111) have shown that the last two monolayers of Mg only desorb at temperatures above 620 K.[16] The model is thus valid for $T < 620$ K. The rate constants for desorption, k_d, surface bulk transport, k_{sb}, and bulk surface transport, k_{bs}, are given by the expressions

$$k_d = \frac{1}{2}\nu_d \exp\left(-\frac{E_d}{kT}\right), \qquad (5)$$

$$k_{sb} = \nu_{sb} \exp\left(-\frac{E_{sb}}{kT}\right), \qquad (6)$$

$$k_{bs} = \frac{N_s}{N_b}\nu_{bs} \exp\left(-\frac{E_{bs}}{kT}\right), \qquad (7)$$

where the activation energies for desorption, surface-bulk, and bulk-surface transport are denoted by E_d, E_{sb}, and E_{bs}, respectively. The corresponding prefactors, are denoted by ν_d, ν_{sb}, and ν_{bs} and are assumed to have the values calculated by a classical approximation for the low hydrogen concentration limit, $\nu_d = 6 \times 10^{12}$, $\nu_{sb} = 3.5 \times 10^{12}$, and $\nu_{bs} = 7.2 \times 10^{11}$ s^{-1}.[17] It is assumed that the surface density of sites in the transition state for surface-bulk transport is equal to N_s.
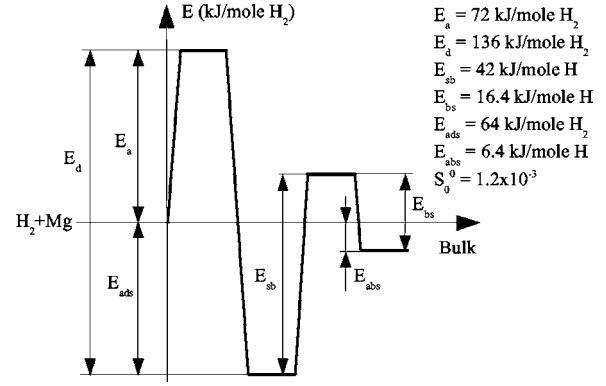

FIG. 4. A schematic energy diagram for the model.

The model is not sensitive to the value of E_{bs} for realistic parameter values. A calculated value for E_{bs} of 16.4 kJ/mole H was used.[17]

An initial film thickness of 400 Å corresponds to $n_l = 150$ ML. The model gives an excellent description of the TPD curve for Mg, as shown in Fig. 2.

The parameter values $S_0^0 = 1.2 \times 10^{-3}$, $E_a = 72$ kJ/mole H_2 and $E_{sb} = 42$ kJ/mole H were obtained simultaneously by minimization of the deviation between calculated and measured hydrogen uptake. The desorption energy, E_d, was adapted to yield the correct temperature for the onset of hydrogen desorption. A value of 136 kJ/mole H_2 was chosen. The shape of the hydrogen peaks can be expected to be influenced by changes in the heat of adsorption of hydrogen which occur for Mg film thicknesses below 15 ML.[16] Such effects are not included in the model. The parameters resulting in the best fit between experiments and model are shown together with the resulting energy diagram in Fig. 4. Values for S_0 calculated from Eq. (2) are plotted in Fig. 3 for comparison with the values for Pt/Mg. The spread in the uptake data gives an uncertainty in S_0 of 40%. If S_0 for 408 K is kept constant by adjusting S_0^0, the uncertainty in E_a is about 15 kJ/mole H_2. The errors in E_{sb} and E_d are estimated to be 2 kJ/mole H and 4 kJ/mole H_2, respectively.

A sizeable discrepancy is found between the value obtained for E_a, 72 ± 15 kJ/mole H_2, and the values of 110 and 100 kJ/mole H_2 calculated by Vegge and Du *et al.*, respectively.[17,21] The difference can perhaps be explained by the presence of step sites which have a lower barrier for dissociation than terrace sites. Such effects have been observed for several diatomic dissociation reactions.[4,22] We have, in the current undertaking, not investigated the exact structure of the Mg overlayer. The value found for E_{sb}, of 42 ± 2 kJ/mole H, is in reasonable agreement with published theoretical values of 48 kJ/mole H.[17,19]

The energy diagram in Fig. 4 shows a heat of absorption for H in the bulk, E_{abs}, of 6.4 kJ/mole H. This value must be considered as an estimate. We believe that the experiments performed with the pure Mg films were made in the α-phase concentration region, since the maximum H/Mg ratio achieved in these experiments is approximately 2%, and uptake experiments performed with Pd activated Mg films show that hydride formation starts at a H/Mg ratio close to 2%.[15] Also, XPS spectra for thin magnesium films on

Mo(111), with H concentrations 10 times higher than what was achieved in this study reveal clear evidence of formation of the hydride (β) phase.[16] XPS spectra for the magnesium films used in this study with a H/Mg ratio below 1% show no indication of magnesium hydride. A value for the heat of absorption for the α phase of 22 kJ/mole H has been reported.[23] From experiments on Pd activated Mg films, Krozer *et al.* conclude that the heat of absorption is less than 12 kJ/mole H.[15]

To summarize, the initial sticking coefficient for molecular hydrogen on pure magnesium has been measured and is found to have a prefactor of approximately 1.2×10^{-3} and an activation barrier for adsorption of 72 ± 15 kJ/mole H_2. From Eq. (2), this corresponds to an initial rate of 0.009 ML H/s at $p_{H_2} = 4$ bar and $T = 433$ K, demonstrating the extremely slow hydrogen dissociation rate on the Mg surface under conditions relevant for hydrogen storage. The stagnant uptake observed for the pure magnesium films containing less than 2% hydrogen is due to the formation of a surface hydride with a heat of adsorption, E_{ads}, of about 64 kJ/mole H_2. The apparent activation barrier for adsorption on the Pt catalyzed films is significantly lower than on pure Mg. No saturation in the uptake rate is observed for Pt/Mg. This can be explained if it is assumed that Pt acts as a bridge between the surface and the Mg bulk, so that the low energy Mg surface sites can be bypassed. Hence, the addition of small amounts of Pt to the Mg surface both increases the sticking coefficient and decreases the influence of self-blocking caused by the formation of surface hydride.

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