Equilibrium hydrogen uptake and associated kinetics for the Mg-H$_2$ system at low pressures

LETTER TO THE EDITOR

Equilibrium hydrogen uptake and associated kinetics for the Mg–H₂ system at low pressures

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Abstract. The hydrogen concentration in Mg in equilibrium with H_2 gas, and the associated kinetics, were measured at 10^3–10^5 times lower pressure than previously reported, by using UHV-prepared Mg samples with a thin Pd coating. Equilibrium can be established above a (pressure-dependent) critical temperature below which interface hydride formation at the Pd/Mg interface prevents equilibration. The new equilibrium data agree well with extrapolations of the high-pressure data. Absorption and decomposition isotherms in the β-phase (plateau region) show large hysteresis. The kinetics results in the α-phase deviate from Sieverts' law near the α–$\alpha + \beta$ phase boundary.

The interaction of hydrogen with metals is frequently studied in surface physics, condensed matter physics, materials science and heterogeneous catalysis. The reason is obvious: hydrogen–metal systems are often ideal model systems for basic studies of surface and solid phenomena and are technologically important in e.g. material processing, hydrogen embrittlement, catalytic reactions, and hydrogen storage in metal hydrides.

Many metals absorb considerable amounts of hydrogen when exposed to H_2 gas [1, 2]. At low concentrations, $\leqslant 0.1$–1%, hydrogen atoms are dissolved in the metal lattice (α-phase) as non-interacting impurities. At somewhat higher concentrations, H–H interaction may appear, but with hydrogen still in solution. At a critical concentration, the 'solvus', a new ordered phase, often called the β-phase (hydride phase), precipitates in many hydrogen–metal systems. The α- and the β-phases may co-exist over a considerable concentration range until, ideally, the whole solid is transformed into the metal hydride phase. It is of basic as well as technological importance to obtain correct equilibrium properties of these systems [3, 4], such as relationships between hydrogen pressure (p), composition (H/metal ratio) and temperature (T), from which more fundamental properties may be evaluated (heat of formation, enthalpy of (phase) transformation, solubility, etc). The kinetics by which hydrogen is absorbed or desorbed also receives considerable interest [5–7], but much less is known about the kinetics than about thermodynamic properties.

Studies on Pd-covered Nb [7] and on pure Pd [8] demonstrate that new and valuable information about metal–hydrogen systems may be obtained on ultra-high-vacuum (UHV) prepared samples subject to surface spectroscopic control. Our data are to our knowledge the first such data for the Mg–H system. We have measured the hydrogen equilibrium uptake and associated kinetics for UHV-prepared, palladium-covered, magnesium films in the temperature range 260–360 K and pressure range 0.03–30 Torr. This regime has been considered inaccessible for studies of the Mg–H system due to its low
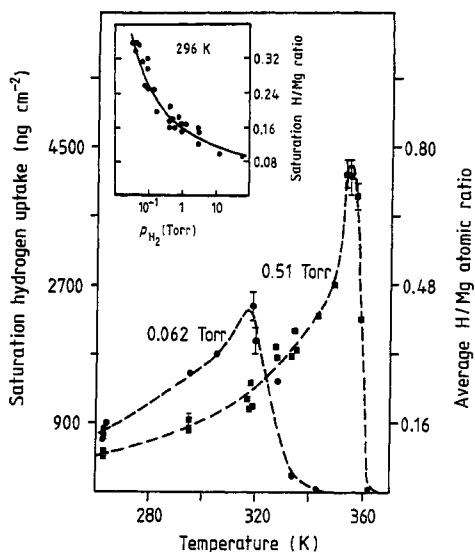
Figure 1. Saturation hydrogen uptake by Pd-coated Mg versus T at 0.062 and 0.51 Torr. Around the maxima the uptake changes from being kinetically limited due to interface hydride formation to being in thermodynamic equilibrium at temperatures above the maxima. The pressure dependence of the saturation uptake in the kinetically limited regime is shown in the inset. The p, T-values at the maxima (■) are plotted in figure 3.

reactivity. Previous studies have been performed at much higher pressures, typically ten to hundreds of bars, and temperatures >500 K [9, 10]. Possible causes for the low reactivity of the Mg–H system are: (i) a large activation barrier for H_2 dissociation [11], (ii) formation of a surface [6, 10] or interface hydride [7, 12] and/or (iii) influence from surface impurities [13].

Recently [12] we used Pd evaporated on top of Mg samples to promote hydrogen uptake at 296 K. Attainment of thermodynamic equilibrium was, however, prevented by the formation of an interface hydride at the Pd/Mg interface, which gives rise to a peculiar pressure dependence; the saturation uptake *decreases* with increasing hydrogen pressure (see the inset of figure 1). In this work we find by exploring the T-dependence of the hydrogen uptake (figure 1),that there is a critical line in T–p space where the hydrogen saturation uptake in Mg changes from being kinetically controlled to thermodynamic equilibrium. The latter finding enabled us to measure equilibrium data for the Mg–H system at lower temperatures and 10^3–10^5 times lower pressure than previously reported.

The experiments were performed in a UHV system [12, 14] equipped with AES/XPS spectroscopy and an elevated-pressure reaction cell for hydriding [15]. Samples were prepared by evaporating Mg films 800 nm thick on a quartz crystal microbalance (QCM) [16], followed by evaporation of a Pd film 7.5 nm thick on top of the Mg film. The cleanliness of the sample surfaces was controlled by AES. Hydrogen uptake was monitored by measuring the frequency decrease (=mass change) of the QCM. The accuracy of the present measurements is ± 4 ng cm^{-2} (± 1 monolayer of H). Influences of pressure on the eigenfrequency of the QCM was compensated for by calibration runs for each crystal. The temperature and pressure accuracies were ± 3 K and ± 0.002 Torr, respectively. After a hydrogen uptake run the sample was completely dehydrided in vacuum at 330 K. The equilibrium results are not sensitive to the Mg film thickness, nor to the choice of electrode material on the QCM. The uptake by the 7.5 nm Pd film is negligible compared with the uptake in Mg.

The kinetics results, especially the conditions for interface hydride formation, will be discussed first, followed by a presentation of the equilibrium data. Figure 1 shows the

saturation uptake as a function of temperature at two different pressures, 0.062 and 0.51 Torr. Each experimental point corresponds to the saturation uptake at constant temperature of a freshly deposited or fully dehydrided sample. At low temperatures the saturation uptake is much smaller than the expected equilibrium value and has the p-dependence shown in the inset of figure 1. This behaviour is caused by nucleation and growth of an interface hydride at the Pd/Mg interface [12], which effectively prevents further uptake, since hydrogen diffusion speed through the hydride is slow [10, 17]. The interface hydride formation has recently been verified and investigated by hydrogen depth profiling [18]. As the temperature is increased the saturation uptake increases, because the interface hydride grows more slowly to form a coherent film [18]. The saturation uptake continues to increase with temperature until a maximum is reached, and then decreases rapidly. The maximum corresponds to the p, T condition where the uptake changes from kinetic to thermodynamic control (see figure 3, full squares, below). At temperatures above the maximum an interface hydride is no longer formed. The dotted area in figure 3 defines the region where equilibrium data for Pd-covered Mg *cannot* be obtained due to interface hydride formation.

We have thus found a region in p–T space where equilibrium data for Mg–H_2 may be obtained. The low-temperature limit of this region is determined by the temperature where interface hydride formation occurs. The high-temperature limit is given by the temperature where interdiffusion and alloying between Pd and Mg takes place. The latter was shown by AES to be negligible below 370 K, but occurs rapidly above 410 K [14].

Equilibrium absorption isotherms were obtained in the p, T range just defined, by raising the hydrogen pressure in small steps and allowing the system to equilibrate after each pressure increase. Results from a typical run are shown in figure 2. Three regimes with different kinetic behaviour were distinguished. At the lowest pressures (<0.36 Torr at 353 K) the uptake is very fast (not shown in figure 2(a)) and equilibration is essentially instantaneous, demonstrating rapid hydrogen diffusion. In the next region (0.36–0.40 Torr at 353 K) the uptake is considerably slower. The uptake rate is fastest immediately after the pressure rise, and then decreases monotonically. Possible reasons for the slower kinetics are discussed below. These two regions both belong to the α-phase region.

At a critical pressure (0.41 Torr in figure 2) the uptake kinetics changes dramatically; the initially slow uptake accelerates (rather than saturates) at constant p. The rate of hydrogen uptake varies here as $m_H^{2/3}(t)$, where $m_H(t)$ is the mass of hydrogen in the sample at time t, as expected for initial nucleation and subsequent 3D growth of hydride nuclei throughout the sample (since the total area of all nuclei is proportional to $m^{2/3}$). This transition in kinetics reflects the transition from the α-phase region to the $\alpha + \beta$-phase region, i.e. the plateau pressure is reached. The plateau pressure for *absorption* is thus 0.41 Torr at 353 K. In figure 3 a set of such p–T plateau values for absorption is plotted in the usually employed $\log p$ versus $1/T$ plot [3].

The uptake showed no sign of decline after the plateau pressure was reached, but instead continued to accelerate. To avoid film cracking the uptake was usually not followed beyond H/Mg ratios of about 0.3. Over this range we did not resolve any variation of the plateau pressure with H/Mg ratio. We estimate an upper limit for the inclination of the plateau of $\Delta p/p \leqslant 4.5\%$ at 353 K.

To obtain the plateau pressure for decomposition the pressure was lowered by successive pressure reductions. Initially the uptake continued in spite of the pressure decrease, although at a lower rate, but eventually a pressure was reached when neither
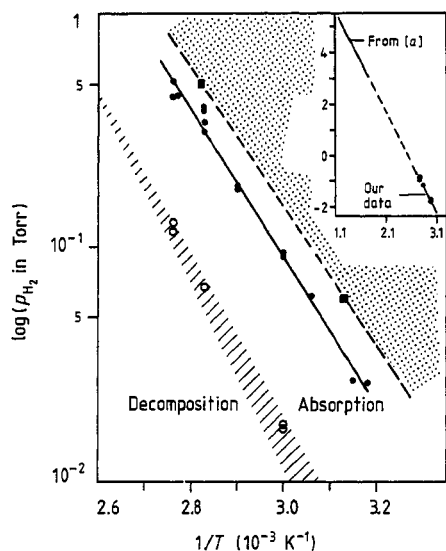
Figure 2. (*a*, *b*): hydrogen uptake versus time at successively higher pressures. Note the acceleration in the uptake when the $\alpha + \beta$-phase region is entered. The uptake to saturation at pressures below 0.38 Torr (not shown) is fast (<30 s). (*c*): equilibrium uptake versus $p^{-1/2}$ in the α-phase.
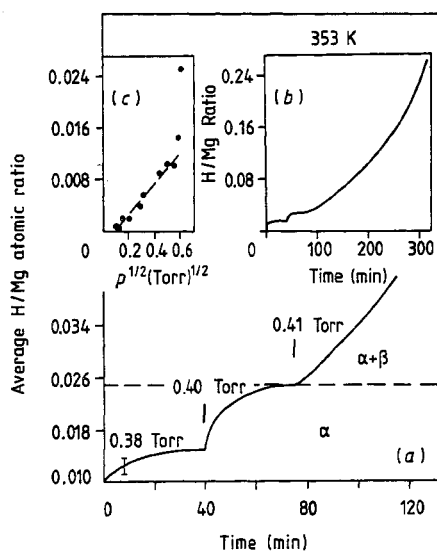
Figure 3. Log of equilibrium (plateau) pressures versus $1/T$. (●) absorption, (○) decomposition, (■) values from the maxima in figure 1. In the dotted part of the figure the system is kinetically limited, i.e. equilibrium is not reached. The inset and the dashed area compares our data with the data obtained at about 10^5 times higher pressure [7].

uptake nor decomposition occurred. This pressure is the plateau (dissociation) pressure for hydride *decomposition*. Further pressure reduction caused net desorption. Figure 3 shows a set of decomposition pressure versus temperature data (open circles). They lie on a straight line in the $\log p$ versus $1/T$ plot, shifted to considerably lower pressures than the uptake line, thus demonstrating a large hysteresis [19] between uptake and decomposition for the Mg–H system at the low temperatures employed in the present case. In [9] the hysteresis for the Mg–H system at considerably higher temperatures was barely discernible and could not be quantified.

From the slopes of the $\log p$ versus $1/T$ plots we obtain enthalpies for the α-to-β phase transformation of 60.7 ± 6.3 kJ (mole H_2)$^{-1}$ and 71.2 ± 4.2 kJ (mole H_2)$^{-1}$, from the formation and decomposition plateaus, respectively. The latter value agrees very well with the value given in [9]. Our new (decomposition) plateau p, T data extend the range of such data by five orders of magnitude in pressure, as shown in the inset of figure 3. The hatched area in the main figure is an extrapolation of the previous high-pressure [9] data including extrapolation errors. The $\log p$ versus $1/T$ plot is within experimental accuracy linear over seven orders of magnitude in pressure.

We now turn to the low-uptake, α-phase region. (The data accuracy is here lower than in the β-phase due to smaller uptakes and larger overall data spread.) The equilibrium uptake is here commonly observed to obey a $p^{1/2}$-dependence (Sieverts' law [3]), as expected for non-interacting H atoms in solution with Mg metal. Figure 2(*c*) shows that Sieverts' law is approximately obeyed up to 0.36 Torr, where a breakpoint is observed after which the concentration increases faster than $p^{1/2}$. Deviation from Sieverts' law has been observed for several H/metal systems, e.g. Pd [3] and Nb [1, 2, 20], and has been attributed to attractive H–H interaction [1, 2, 4]. Suggested mechanisms for

such interaction are the continuous lattice expansion accompanying increasing hydrogen concentration, which causes lattice-mediated H–H interaction and/or electronic interaction [1, 4, 21]. Such interaction gives rise to the formation of local hydrogen-rich 'clusters' as reported for the Pd–H [1] and Nb–H [20] systems, which may be regarded as precursors to the formation of stable hydride nuclei. The attractive H–H interaction could explain the slower kinetics observed in the range 0.36–0.40 Torr at 353 K, since it would reduce hydrogen mobility.

After the breakpoint in figure 2(c) the system is still in the α-phase. The α–$\alpha + \beta$ borderline is reached when the kinetics changes to an accelerating uptake rate at constant pressure as discussed above. In the data of figure 2 this occurs at a H/Mg atomic ratio of 2.6×10^{-2}. The mean value from several measurements for the solvus at 353 K is, however, $1.8(\pm 0.8) \times 10^{-2}$, which illustrates the relatively large data spread at low uptakes mentioned above. The solvus concentration increases with increasing temperature, but this has not yet been quantified.

We summarise our results as follows. Pd coating of Mg allows hydrogen uptake measurements and Mg–H_2-gas equilibration at low pressures and temperatures. At too low temperature (too high pressure) an interface hydride nucleates at the Pd–Mg interface and grows to a continuous film preventing further uptake and attainment of thermodynamic equilibrium. The passivation occurs at smaller uptakes the higher the pressure, at constant T. At suitable combinations of p and T complete equilibration between the H_2 gas and the solid α,β-phases is possible. In the dilute limit the uptake obeys Sieverts' law. At higher concentrations in the α-phase, up to the solvus around $\leqslant 2$ at.%, stronger than $p^{1/2}$-dependence and slower kinetics are observed, tentatively attributed to attractive H–H interaction. The plateau region shows strong hysteresis effects between absorption and decomposition. The $\log p$ versus $1/T$ relation for the decomposition plateau pressure is linear over seven decades and yields an enthalpy of phase transformation of 71 kJ (mole $H_2)^{-1}$.

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