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In-situ Study of Hydriding Kinetics in Pd-based Thin Film Systems

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Abstract

The hydriding kinetics of Pd thin films has been investigated in detail. The key experimental technique used in this work consists of a high resolution curvature measurement setup, which continuously monitors the reflections of multiple laser beams coming off a cantilevered sample. After mounting the sample inside a vacuum chamber, a H-containing gas mixture is introduced to instantaneously generate a given hydrogen partial pressure (p_{H2}) inside the chamber. The resulting interaction of H with the Pd layer then leads to a volume expansion of the thin film system. This induces in turn changes in the sample curvature as a result of internal stresses developing in the Pd film during a hydriding cycle. Based on such curvature date obtained in-situ at different p_{H2}, a two-step model for the kinetics of Pd-hydride formation has been proposed and expressions for the hydrogen adsorption and absorption velocities have been derived. The rate-limiting steps have been identified by studying the p_{H2}-dependence of these velocities. Furthermore, from our in-situ experimental data, relevant kinetic parameters have been calculated. The effect of dry air exposure of the Pd films on the hydriding kinetics has been considered as well.

1 Introduction

Among the major obstacles to the technological reconversion of mobility and transport applications towards green and sustainable hydrogen technologies are a number of issues related to H-storage [1, 2]. Solid-state hydrogen storage is the most promising solution since its potential in terms of hydrogen volume and weight density is higher than that of conventional tanks [3 - 5]. The storage issues related to the wide family of solid-state hydrides can be classified as thermodynamic and kinetic issues [6]. On-board storage applications require restrictive operation temperature and pressure ranges. The reversibility of hydriding is another critical parameter. This requirement implies low driving forces for both hydriding and dehydriding reactions, thus usually poor kinetics.

In this context, the hydrogen-palladium system is a good model system in view of the design of effective hydrogen storage materials. Indeed, the Pd hydriding mechanism is fast, spontaneous and reversible at room temperature. It has been the most extensively studied hydrogen-metal system for more than a century [7]. Nevertheless, the Pd hydriding mechanism is still an issue of debate, especially regarding its kinetic details [8, 9].

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In this respect, this work focuses on a more detailed understanding of the hydriding kinetics of the Pd-based model system. The kinetic model presented here takes into account the mechanisms of adsorption and absorption of hydrogen into the Pd lattice. This extended abstract will first focus on the main ideas from which the kinetic model has been built. It will then elaborate an identification of the rate-limiting steps of the Pd hydriding mechanism and the calculation of relevant kinetic parameters (bulk and surface coverage) from in-situ hydriding curves obtained at different p_{H2}. Finally, the effect of long-term dry air exposure of the samples on the hydriding kinetics is discussed as well.

2 In-situ Measurement Principle

The experimental setup considered for our in-situ approach, as well as the sample characterization, are already described in detail in another publication [10]. The samples used here were cut approximately 3x0.5 cm^2 in size from two oxidized, 425 µm thick Si wafers. These were coated by e-gun evaporation with a pure Pd thin film on top of a 5 nm thick Ti adhesion layer. The Pd thin film thicknesses and the initial stresses in those films after deposition have been characterized for two different batches and are listed in Table 1. The error is on the order of 1% for the thickness measurements and 0.1% for the initial stress measurements. The table also mentions the approximate time spent by the samples in the desiccator between their deposition process and their cycling with hydrogen.

Table 1: Sample characterization of the palladium films.

	Sample 1	Sample 2
Pd thickness [nm]	128	112
Initial stress level [MPa]	435	409
Dry air exposure time [months]	12	2

The cantilevers obtained this way are embedded in a vacuum chamber, with a base pressure on the order of 10^{-6} mbar. A ultra-pure Ar/H$_2$ gas mixture is then instantaneously introduced into the chamber in order to impose a desired p_{H2}. The sample curvature is measured in-situ with a high resolution curvature measurement setup, including a laser beam source mechanically fixed onto the chamber. A CCD camera mounted onto the chamber continuously detects the position of 5 laser beams reflected off the cantilevered sample, allowing to monitor the sample curvature $\Delta\kappa$ in real time. The internal compressive stresses developing in the Pd film during hydriding are a result of the prohibited volume change during Pd-H interaction in the thin film geometry. They can be deduced from the measured changes in the sample curvature thanks to Stoney's equation [11].

3 Results and Discussion

The four major steps involved in Pd hydriding are H$_2$ molecular adsorption, dissociative chemisorption, atomic hydrogen diffusion and finally hydride formation. The present kinetic model considers two main steps, as inspired from Wagner's seminal work [7]. The first step, called here "adsorption", involves H$_2$ molecular adsorption and dissociative chemisorption. Diffusion and hydriding constitute the second step, called here "absorption". In fact, the absorption step does not take explicitly into account the hydrogen diffusion mechanism. Indeed, it can easily be shown that bulk diffusion can be considered to be non-rate limiting in our thin film geometry [10]. The adsorption and absorption reactions and their equilibrium constants are presented in Eqs. (1) - (4):

$$H_2 + 2s \Leftrightarrow 2H - s \tag{1}$$

$$K_{ad} = \frac{k_{ad}^{'}}{k_{ad}^{''}} = \frac{\theta_{eq}^2}{(1-\theta_{eq})^2} \frac{1}{p_{H_2}} = \frac{1}{K_S^2} \tag{2}$$

$$H - s + i \Leftrightarrow H - i + s \tag{3}$$

$$K_{ab} = \frac{k_{ab}^{'}}{k_{ab}^{''}} = \frac{1-\theta_{eq}}{\theta_{eq}} \cdot \frac{n_{eq}}{1-n_{eq}} \tag{4}$$

Here, s is a surface adsorption site and i is a bulk absorption site. θ_{eq} and n_{eq} are the equilibrium surface coverage and bulk H/Pd atomic ratio, and K_s is the well-known Sievert's constant describing the ideal solution behavior [7].

Starting from those expressions, a kinetic model has been built according to two main hypotheses. Firstly, it is assumed that θ reaches values close to θ_{eq} much before n reaches its equilibrium value. This reasoning leads to the following expressions for the adsorption and absorption velocities:

$$\frac{d\theta}{dt} = \overbrace{\left[k_{ad}^{'}(1-\theta)^2\right]}^{S_{ad}} \cdot p_{H_2} \overbrace{- k_{ad}^{''}\theta^2}^{I_{ad}} \tag{5}$$

$$\frac{dn}{dt} = \overbrace{\left[\frac{k_{ab}^{'}}{K_S}\left[1 + n\left(\frac{1-K_{ab}}{K_{ab}}\right)\right]\right]}^{S_{ab}} \cdot \sqrt{p_{H_2}} \overbrace{- k_{ab}^{''} n}^{I_{ab}} \tag{6}$$

Secondly, every parameter in Eqs. (5) and (6) is assumed to be independent of p_{H2} (and hence, so are the slopes S_{ad} - S_{ab} and the intercepts I_{ad} - I_{ab}). This second statement is inspired from experimental observations [10]. As seen in Figure 2, two linear kinetic regimes are observed during hydrogen loading of our samples. The latter are separated by a brutal, instantaneous transition. As shown in Figure 1, these constant slopes further exhibit a linear relationship with respect to $\sqrt{p_{H2}}$ in the first regime, and vary linearly with p_{H2} in the second regime.

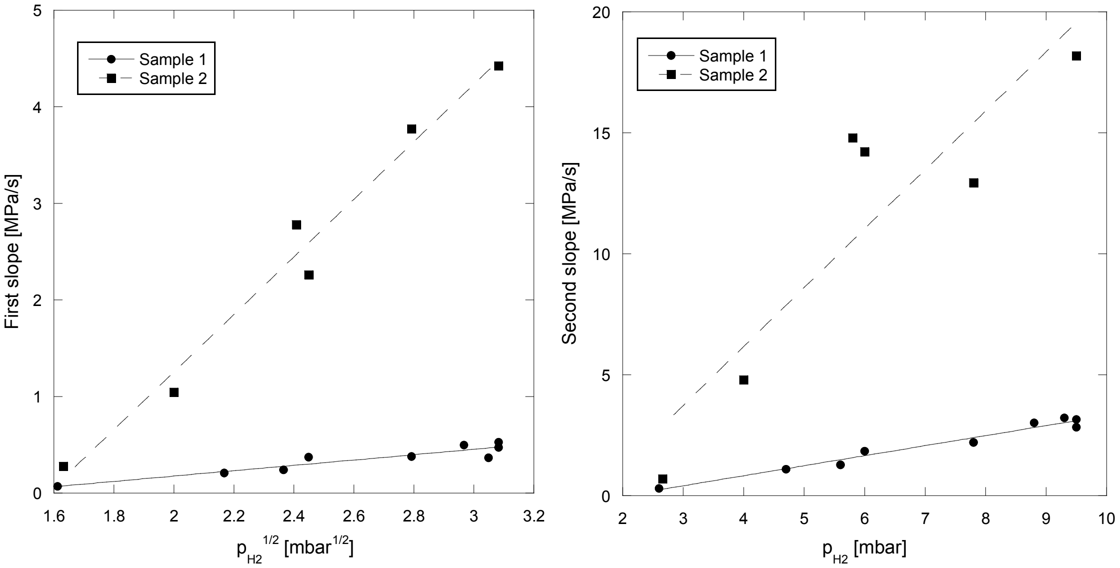

Figure 1: First and second slopes as functions of $\sqrt{p_{H2}}$ and p_{H2}, respectively.

Moreover, the effect of dry air exposure time clearly appears in Figure 1. The more important is this time interval, the slower is the hydriding kinetics. This effect is attributed to a long-term chemical reaction between the Pd surface and oxygen in air, which is believed to affect the initial palladium surface coverage [7].

All the experiments presented here have been carried out in the α phase region of the Pd-H phase diagram ($p_{H2} < 10$ mbar [10]). In this phase, the equilibrium compressive stress levels are located between 300 and 500 MPa, thus leading to exclusively elastic deformation if one takes into account the initial tensile stresses in the Pd films (cfr. Figure 2). Consequently, the measured stresses are directly proportional to the hydrogen concentration in the fcc palladium lattice [12]. If t_{tr} is the transition time between the linear kinetic regimes, one can then write:

$$t_{tr} \propto \frac{1}{S_{ad}\, p_{H_2} - S_{ab}\sqrt{p_{H_2}} + \left(I_{ad} - I_{ab}\right)} \tag{7}$$

Taking the calculated slopes and intercepts from sample 2 as an example, observations from Figures 1 and 3 confirm that the first kinetic regime is limited by absorption and the second one by adsorption. Indeed, if one assumes the contrary statement, the resulting reasoning would lead to the opposite function in Eq. (7) and therefore to the prediction of negative transition times, which is physically impossible.

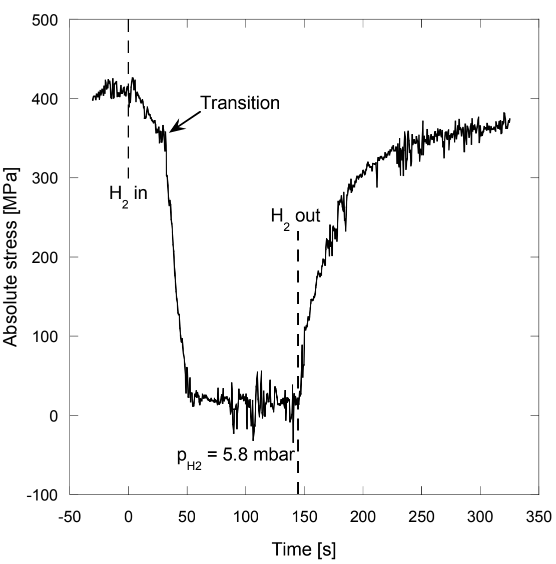

Figure 2: **Typical hydriding cycle (sample 2).**

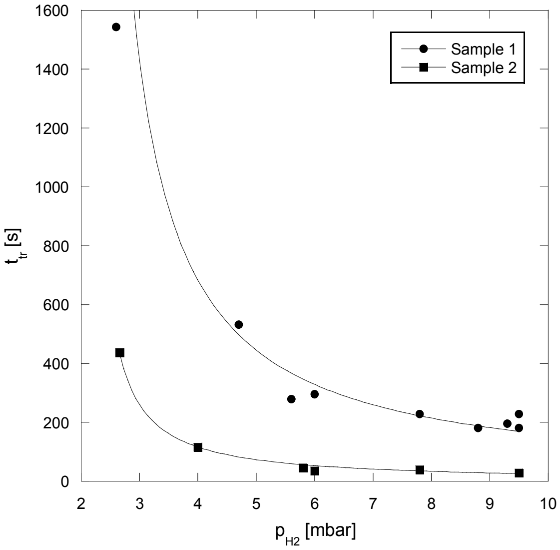

Figure 3: **Transition times as functions of p_{H2} fitted with Eq. (7).**

Moreover, if one takes the value of K_s already calculated in [10] and assumes that K_{ab} = 1 (so $n_{eq} = \theta_{eq}$), the resulting calculation from Eqs. (5) and (6) gives $\theta = 3.4.10^{-3}$ in the second kinetic regime and $n = 3.5.10^{-3}$ in the first kinetic regime. Those values make sense because they are indicative for bulk H-concentrations corresponding to the α phase region of the palladium hydride [7].

4 Conclusion

The quantitative analysis of in-situ recorded hydriding cycles according to our kinetic model enabled to identify the rate-limiting steps of Pd hydriding and to calculate surface coverage and bulk H/Pd atomic ratios in the α phase of the Pd hydride. The first linear kinetic regime is limited by absorption and the second one is limited by adsorption. The samples presented here have been compared in terms of dry air exposure time. The results show a strong influence of this parameter on the hydriding kinetics. The slowing down of the kinetics is attributed to a partial occupation of the palladium surface by oxygen. Further characterization is necessary in order to identify the chemical nature of the surface.

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