Hydrogen detection in metals: a review and introduction of a Kelvin probe approach

Stefan Evers, Ceylan Senöz and Michael Rohwerder

Christian-Doppler Laboratory for Diffusion and Segregation Phenomena, Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Strasse1, D-40237 Düsseldorf, Germany

E-mail: rohwerder@mpie.de

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Abstract

Hydrogen in materials is an important topic for many research fields in materials science. Hence in the past quite a number of different techniques for determining the amount of hydrogen in materials and for measuring hydrogen permeation through them have been developed. Some of these methods have found widespread application. But for many problems the achievable sensitivity is usually not high enough and ready-to-use techniques providing also good spatial resolution, especially in the submicron range, are very limited, and mostly not suitable for widespread application. In this work this situation will be briefly reviewed and a novel scanning probe technique based method introduced.

Keywords: hydrogen, permeation, Devanathan–Stachurski, Kelvin probe

1. Introduction

Hydrogen in metals is a topic of great importance in materials science. Its presence in metals may be wanted or unwanted. For instance, hydrogen may be of central importance as an energy carrier of the future. If so, its production, controlled storage and release, as well as its safe transport will become crucial issues. For this application its uptake into metals, to form metal hydrides, and its release from these hydrides would be desired to be as effective as possible [1–5].

Another application where hydrogen in metals is desirable is the so-called thermo hydrogen processing (THP). THP may enhance processing behavior and final component characteristics of e.g. Ti-based alloys [6–11], although for commercial purity titanium this is still controversial [12].

In this process, hydrogen is added to the titanium alloy by exposing the material at a relatively high temperature to a hydrogen-containing atmosphere, performing heat treatment and/or the desired thermomechanical processing, and then removing the hydrogen, e.g. by a vacuum or inert gas anneal. Its presence is claimed to possibly allow titanium alloy to be processed at lower stresses and to be heat-treated to produce novel microstructures with enhanced mechanical properties.

However, in most cases hydrogen in metals is unwanted, as even in very low concentrations it can cause so-called hydrogen embrittlement in many steels and other alloys, which constitutes a serious safety and performance problem e.g. in constructions, planes and medical implants [13–32].

The tiniest amounts of hydrogen can cause hydrogen embrittlement and sometimes delays to fracture of days or even months or more are observed. For an in-depth understanding of the underlying phenomena reliable detection of hydrogen at ultra-low levels well below the ppm range is of crucial importance. As hydrogen can be taken up by the metal during its processing, such as e.g. annealing, pickling or other cleaning steps, but also at later stages during its application, such as due to corrosion or cathodic corrosion protection, it is also important to be able to measure its uptake and diffusion as sensitively as possible. So far mainly the so-called diffusible hydrogen has been identified as the main factor leading to hydrogen embrittlement, see e.g. Akiyama et al [33, 34]. However, as most laboratory tests are
performed on a relatively short time scale, it remains unclear as to how far hydrogen from (at least not too deep) trap sites may play a role over longer time spans, as this hydrogen may also diffuse to sites, initiating embrittlement. For a detailed fundamental understanding of the underlying mechanisms a full characterization of the microstructure and knowledge of the amount of hydrogen in the material, its distribution on the micro- and macro-scale, as well as its binding states and of possible sources of hydrogen, is of crucial importance.

Techniques such as melt extraction of hydrogen do not distinguish between hydrogen bound at different trapping sites and may also lead to erroneous detection of hydrogen stemming from hydroxides or other sources instead of hydrogen in the material [35]. Thermal desorption spectroscopy (TDS) is a more advanced technique, allowing one to determine the binding energies of the differently bound hydrogen [36–42], but does not provide spatial resolution.

There are also a few spatially resolving techniques available. For highly sensitive depth profiling, down to a few microns, nuclear reaction analysis (NRA) can be utilized, which provides sensitivity in the ppm range and a vertical depth resolution in the nanometer range [43]. Lateral spatially resolving methods are e.g. the tritium autoradiography or microcontact printing. In tritium autoradiography the samples of interest are loaded with hydrogen isotopes that are rich in tritium and then coated by a sensitive film of photographic nuclear emulsion made of fine silver bromide grains. The specimens are then placed in a dark box under a nitrogen atmosphere where β-rays emitted from the tritium decompose the silver halides in the film. After chemical treatment with a suitable developer the specimens are then observed by SEM or TEM. With this technique the accumulation of hydrogen along slip bands, grain boundaries and second phase particles has been revealed [44–47]. For safety reasons all mobile tritium is usually outgassed prior to the measurement. Hence only strongly bound hydrogen is measured. A related technique, measuring hydrogen that is mobile, is so-called hydrogen microcontact printing. Here the silver ions are directly reduced to metallic silver by the hydrogen from the specimen [48]. With this technique enhanced hydrogen diffusion under a stress gradient and accumulation at stress concentrated areas can be shown [49, 50].

Really high sensitivity techniques with high spatial resolution are, however, still lacking.

A new approach, based on the Kelvin probe technique, will be discussed in the following, after briefly reviewing in more detail the electrochemical Devanathan–Stachurski method, which sets the current standard and, as will be shown, can be directly compared to the new method.

The Devanathan–Stachurski permeation cell is an electrochemical double cell set-up where both sides of the sample, cut to a sheet of appropriate size, form the electrode in one of the two cells [51, 52].

In one cell the sample is potentiostatically or galvanostatically charged with hydrogen (entry side). In the other cell the other side is polarized anodically so that the permeating hydrogen is fully oxidized (exit side), the anodic current providing direct information about the hydrogen permeation. On the exit side the sample is usually coated by a thin layer of palladium in order to avoid too high noise levels by oxidation currents of the sample material and to ensure high catalytic activity for the hydrogen oxidation reaction. The entry side is either also covered by palladium, if the focus is on the permeation of hydrogen in the material, in order to ensure well defined hydrogen activity on the entry side, or uncoated, if the focus is on the hydrogen uptake, such as e.g. under corrosion conditions.

This Devanathan–Stachurski method is a powerful tool for investigating hydrogen in steels and other alloys, since it provides information not only about diffusion constants of hydrogen in materials, but also about density of trap sites and trap energies. This becomes directly obvious when considering the presumably simple case of hydrogen diffusion through high purity iron. Riecke and Bohnenkamp [53] evaluated literature data of experimentally derived diffusion coefficients for pure iron, in dependence on temperature [53–55]. Only at higher temperatures are the values from different works close to each other; at room temperature differences in the order of three magnitudes are observed. This is a direct result of the interaction of hydrogen dissolved interstitially in the crystal lattice and lattice defects in the iron, such as vacancies, foreign atoms, dislocations, grain boundaries, voids and other defects [53]. Most of these defect sites tend to react exothermally with interstitial hydrogen, as opposed to the endothermic dissolution of hydrogen in the lattice [56], and constitute traps for hydrogen uptake, respectively sources for hydrogen release. The effective diffusion coefficient of hydrogen in the presence of defect sites is always smaller than that of ideally dissolved hydrogen in the defect-free perfect crystalline lattice. As ideally dissolved hydrogen we consider hydrogen in more or less unperturbed interstitial lattice sites. In bcc iron these are predominantly tetrahedral lattice sites [57].

All other hydrogen interactions with lattice defects and is not regarded as dissolved hydrogen, but more or less strongly bound to the defect sites. The formation of the equilibrium between hydrogen at a defect site \( i \) and dissolved in the lattice is determined by the rates for trapping and release

\[
\frac{\partial c_{Ti}}{\partial t} = k_{trap,Ti}c_L(1 - n_{Ti})N_{Ti} - k_{release,Ti}c_{Ti}(1 - n_L)N_L, \tag{1}
\]

where \( c_{Ti} = n_{Ti} \cdot N_{Ti} \) is the concentration of hydrogen bound in trap sites \( i \) of density \( N_{Ti} \) and \( n_{Ti} \) is their occupation. Accordingly \( c_L = n_L \cdot N_L \) is the concentration of dissolved hydrogen where for bcc iron \( N_L = 0.846 \text{ mol cm}^{-3} \) is the density of tetrahedral lattice sites. The reaction constants \( k_{trap,Ti} \) and \( k_{release,Ti} \) are the reaction constants for trapping in sites \( i \) and release from these sites. Assuming that

\[
K_{Ti} = \frac{k_{trap,Ti}}{k_{release,Ti}} = \exp\left(-\frac{E_{ik}}{RT}\right), \tag{2}
\]

\( n_{Ti} = \beta_i/(1 + \beta_i) \) with \( \beta_i \equiv c_L K_{Ti}/N_L \) and assuming that the density of deep traps is \( N_1 \) and of the more shallow ones \( \sum_{i=2}^{\infty} N_{Ti} \), McNabb and Foster have developed a...
Figure 1. Determination of the time lag \( t_i \) from the measurement of the permeation current density \( I_p(t) \) (\( t_0 \) is called break-through time). \( I_p^S \) is the final current density (saturation current density).

The mathematical model for calculating the time delay for hydrogen permeation through the sample caused by the interaction with the trap sites [58]

\[
\frac{t_f}{t_i} = 1 + \frac{3\alpha_i}{\beta_1} \cdot \left[ 1 + \frac{2}{\beta_1} - \frac{\beta_1}{\alpha_1} (1 + \beta_1) \ln(1 + \beta_1) \right] + \sum_{i=2}^{m} \alpha_i, \tag{3}
\]

where \( t_f \) is the time lag for hydrogen permeation derived according to Boes and Züchner [59] and \( t_i \) the corresponding time for the unperturbed iron lattice (see figure 1). The parameter \( \alpha_i = N_{Ti}/N_{Ti} \) is defined as the product of density of trap site \( i \), normalized by the tetrahedral lattice sites, and the corresponding equilibrium constant.

In the often encountered case that the hydrogen diffusion is mainly affected by shallow traps, e.g. if the deep ones are all occupied, we can use a so-called effective diffusion coefficient \( D_i \), that can be determined with the time lag method from the time lag \( t_i \) and the thickness of the sample \( d \) [53]

\[
D_i = d^2/6t_i.
\]

With the above equation and (3) we can then write [53]

\[
D_i = D_L \left( 1 + \sum_{i=2}^{m} \alpha_i \right)^{-1}. \tag{4}
\]

Based on this, Riecke and Bohnenkamp could show for recrystallized iron that the diffusion constant for perfect lattice is much higher than hitherto expected and that it is influenced only by shallow traps.

If deep traps as well as shallow traps play a role, as e.g. for insufficiently hydrogen-loaded deformed iron, then the hydrogen permeation depends on the hydrogen concentration in the samples and the above equation (3) has to be used. Information about binding energies can be reliably derived from equations (1)–(4) when experiments are performed at different temperatures.

However, for multi-phase materials the evaluation of permeation data is much more complex. Local resolution is required, but so far only to a limited extent provided by available standard techniques, such as the above-described Devanathan–Stachurski method. Novel methods with spatial resolution are, however, approaching.

One recent development that allows the high resolution probing of local hydrogen diffusion is based on nano-indentation atomic force microscopy (NI AFM) [60, 61]. Barnoush et al found that by measuring the delay to tip pop-in when applying a load on the tip that exceeds the limit for the hydrogen charged material, they can obtain highly localized information about the hydrogen diffusion. A pop-in occurs in the load displacement curves at the onset of plasticity, which is lowered by hydrogen [61]. Low dislocation densities are required; otherwise the indenter mainly activates existing sources such as Frank-Read sources, and no pop-ins occur. Since nano-indentation involves small volumes of material, this is usually fulfilled and hence the measurements are performed in the undisturbed material. For increasing loads, the probed volume increases and hence the delay to pop-in. From this calculation of local diffusion constants is possible [60, 61].

2. The new method: hydrogen detection by a Kelvin probe

2.1. Introduction

Also based on AFM are the first works on highly resolved hydrogen detection by scanning Kelvin probe force microscopy (SKPFM) [62]. Senöz et al [62] describe how permeation of hydrogen through polycrystalline samples can be studied with high lateral resolution down to the grain boundaries. The observed changes in local work function measured on a duplex steel sample were interpreted as changes in the band structure of the oxide caused by hydrogen [62]. This interpretation is based on the work by Krasemann et al [63], who found that hydrogen reduces Fe\(^{3+} \) states in iron oxide to Fe\(^{2+} \) states. As the Fermi level position of the iron oxide is determined by the ratio Fe\(^{3+} / \)Fe\(^{2+} \) at the oxide surface [64–66], the reduction of Fe\(^{3+} \) states leads to a corresponding change of the work function \( \Psi \) [63]

\[
\Psi (t) - \Psi (t = t_i) = \frac{-RT}{F} \ln \left( \frac{d_{Fe^{2+}}(t)}{d_{Fe^{2+}}(t = t_i)} \right) - \ln \left( \frac{d_{Fe^{3+}}(t)}{d_{Fe^{3+}}(t = t_i)} \right),
\]

where \( t = t_i \) denotes the initial situation before hydrogen has reached the oxide surface. An example for such permeation measurements is shown in figure 2, where hydrogen permeation through different iron oxides of different thickness was measured by a Kelvin probe.

After an initial time lag for permeation through the oxide, a decrease in work function (reported here as electrode potential versus SHE (see also [68, 69])) is indeed observed. However, it is also striking that even for samples with the same kind of oxide film of similar thickness, the observed change
in work function may differ significantly as a function of time as well as in the absolute change ΔW. This is presumably due to the difficulty in preparing reproducibly exact oxide films. Defects in the oxide such as voids and vacancies may have strong effects on the mobility of hydrogen through it, but such parameters are difficult to control. Hence, up to now it has not been possible to obtain information about the correlation between the work function and the amount of hydrogen in the oxide.

Still, as reported by Senöz et al. [62] the change in work function caused by hydrogen can be used to perform measurements of hydrogen permeation with very high spatial resolution. For this they used an atomic force microscope in the Kelvin probe mode, the so-called SKPFM [62, 69–74]. For a duplex steel with ferritic and austenitic grains they could observe the difference in hydrogen permeation through the different phases; even some information about the grain boundaries could be obtained.

In similar studies performed also on a polycrystalline palladium membrane a potential decrease as a consequence of hydrogen permeation was observed [62]. At first the resulting potential changes were believed to be due to the formation of electrochemical equilibrium between the reduction of residual oxygen and hydrogen oxidation at the surface of the palladium, the potential of which decreases with increasing amount of hydrogen reaching the surface [62]. However, as this also worked in an oxygen-free nitrogen atmosphere this was soon found not to be the case. As will be explained in the next section, the work function measured on hydrogen-loaded palladium is somewhat correlated with the hydrogen electrode. Also here extremely high lateral resolution could be successfully achieved by SKPFM [62].

In figure 3 the work function across two grains and the intersecting grain boundary is shown as a function of time after starting the hydrogen loading at the entry side of the palladium membrane. As can be seen, through the upper grain A (of (001) orientation [62]) hydrogen permeates faster than on the lower grain B (of (111) orientation [62]).

Permeation along the grain boundary does not seem to be enhanced here, in accordance with Kirchheim et al. who found that grain boundary diffusion is slower than in the grain at low hydrogen content in the palladium, due to the high trap density at the grain boundaries [75]. The diffusion constant of hydrogen in palladium is more or less the same for the different crystallographic orientations, about $4 \times 10^{-11}$ m$^2$ s$^{-1}$ (see e.g. [76]). Therefore, the difference observed in the permeation behavior through the different grains is most likely due to differences in the trap densities in these grains [62]. Interestingly, figure 3 indicates that lateral cross diffusion may play a role and also that at later stages, when the traps along the grain boundaries are presumably filled, the permeation along the grain boundary starts to get faster than through the grains (see the green line in figure 3).

After a sufficiently long time all mapped grains show a similar potential. As the experiment was performed in a nitrogen atmosphere, i.e. in the absence of oxygen, it is unlikely that the work function measured on the grains is really determined by equilibrium between oxygen reduction and hydrogen oxidation on the palladium surface. Indeed, it was found that the work function measured on palladium containing hydrogen is correlated with the potential of the hydrogen electrode on palladium [77].

2.2. The new method: quantitative hydrogen detection by the Kelvin probe

For palladium fully immersed in electrolyte hydrogen concentrations that are within the concentration range of $\alpha$-Pd–H, i.e. below the concentration where $\beta$-Pd–H, (palladium hydride) is formed, the potential is known to depend logarithmically on the hydrogen concentration in the palladium, following the Nernst equation [78–80]. This seems also to occur on the surface of palladium not immersed in electrolyte, i.e. there is a clear logarithmic correlation between measured work function on the surface of palladium and the amount of hydrogen absorbed in it, if a thin layer of adsorbed water is enabled to form on this surface [77].

Now one might think that measuring hydrogen in palladium is of interest only for a very limited amount of applications. However, how this can be applied far more generally can be seen in figure 4. Shown there is a measurement of the work function over an iron sample that was charged on a spot a few millimeters in diameter using a droplet cell with hydrogen. Afterwards a thin palladium layer about 100 nm thick was deposited on its surface by physical vapor deposition. Since the chemical potential of hydrogen in palladium is much smaller than in iron, hydrogen diffuses out of the iron into the palladium, where it accumulates. Then an SKP measurement is performed, recording a work function map of a surface area of $10 \times 10$ mm$^2$, with the hydrogen loaded area in the middle. As can be seen, the work
Figure 3. Left: consecutive potential maps measured by SKPFM on a thin polycrystalline Pd-foil. Right: cross sectional views of the potentials (indicated by the lines in the potential maps) measured by SKPFM across the grains and the intersecting grain boundary. The arrows indicate the corresponding scan direction of each line. As can be seen, through grain A hydrogen permeation is faster than through grain B. The profile of the red line indicates that there is lateral cross diffusion from grain A into grain B. The green line indicates that at later stages, when the traps in the grain boundary are filled, diffusion along the grain boundary might be enhanced, as now there the work function is decreased the most. A Pd foil of 100 μm thickness with average grain size in the same range or larger was used for the experiment. The grain orientations were characterized by EBSD (see [62]).

Figure 4. Left: map of work function distribution on the surface of a 100 nm thin palladium film evaporated on an iron sample that was locally charged with hydrogen, measured by SKP microscopy in a dry nitrogen gas atmosphere. Right: why it works: since the chemical potential of hydrogen in palladium is much smaller than in iron, hydrogen diffuses out of the iron into the palladium, where it accumulates and thus can be measured by SKP.

The work function of the palladium is significantly decreased above the area where the iron was charged with hydrogen, due to the above-mentioned formation of a hydrogen electrode [77].

According to the Nernst equation we expect for the potential of the hydrogen electrode

\[ E = E_{SHE}^0 + RT/F \ln (a(H^+)/\sqrt{p_{H_2}}). \]

Hydrogen is very soluble in palladium. Hence, equilibrium establishes between adsorbed hydrogen \( H_{ad} \), which in turn is in equilibrium with the hydrogen gas of pressure \( p_{H_2} \), and hydrogen absorbed inside the palladium.

Hence, we can write for the palladium

\[ E = E_{SHE}^0 + RT/F \ln (a(H^+)/a(H_{ad})), \]

where \( a(H^+) \) is the activity of \( H^+ \) in the electrolyte and \( a(H_{ad}) \) the activity of hydrogen absorbed in the palladium, i.e. interstitial, dissolved hydrogen in the palladium lattice.
Figure 5. (a) Measurement of hydrogen permeation through a steel membrane coated on the exit side by a thin palladium layer. The hydrogen reaching the interface between the steel and the palladium directly enters the palladium, because there the chemical potential for hydrogen is much lower, which keeps the concentration at the steel surface close to zero (see sketch on the left-hand side, schematically showing the evolution of the concentration during the permeation experiment: the concentration profile progresses through the steel (dotted lines) until a linear gradient is established (solid line)). The corresponding evolution of hydrogen in the palladium film is schematically shown on the right-hand side. This concentration is equivalent to the passed charge in a standard permeation experiment performed with Devanathan–Stachurski cells. Hence time lag analysis can be directly performed. (b) Measuring hydrogen release from a steel sample by coating it with a thin film of palladium and monitoring the change of work function. Schematically shown is the evolution of chemical potential in the steel ($\mu_{Fe}(H)$) and in the palladium ($\mu_{Pd}(H)$). After an initial period, a constant release rate is established by the formation of a dynamic equilibrium between hydrogen flow into the palladium, release from traps and diffusion to the interface in the finally reached gradient of the chemical potential. The slope of 130 mV per decade of hydrogen concentration, which is different from the 60 mV per decade expected from the Nernst equation, is due to the nanoscopic structure of the palladium film, resulting in a deviation of activity from concentration, see [77].

Hence, at room temperature we would expect a change of the potential by about 60 mV when the concentration of hydrogen is changed by a factor of 10. This is found for hydrogen-charged palladium membranes immersed in viscous sulfuric electrolyte [78], if the palladium is annealed and thus has only a very low density of defect sites such as dislocations. The high viscosity of the electrolyte is required in those experiments in order to limit too fast loss of hydrogen from the palladium into the electrolyte. However, if highly deformed or nano-crystalline palladium membranes are used, then significant deviations from the 60 mV per decade of concentration are observed [81, 82], because then activity and concentration differ significantly.

For evaporated 100 nm films, that are nano-crystalline in nature, we find for the work function a dependence of 130 mV per decade of hydrogen concentration in the film, which accordingly we relate to hydrogen trapped in the grain boundaries in the palladium film and at the interface between the palladium film and the substrate [77].

On surfaces in UHV many processes determine the work function changes caused by hydrogen, such as e.g. severe surface restructuring [83]. Hence, it is not surprising that under UHV conditions we could not find a reliably quantifiable correlation between the work function of palladium and the content of hydrogen in it. This is different for work function measurements of palladium under a dry or humid nitrogen gas atmosphere [77]. As after evaporation of the palladium film the sample is transported to the Kelvin probe through lab air, some water will always adsorb on its surface. Even in dry atmosphere a nanoscopic water layer will prevail, as was shown already for many different cases [84]. Hence, as indicated above, the observed dependence of the work function on hydrogen concentration inside the palladium films has to be due to the formation of a hydrogen electrode on the ‘dry’ surface [77]. For this reason, in the following we refer to the work function as the potential of this hydrogen electrode. This potential will be referenced versus the onset of the formation of the binary phase (bp), below which the potential is no longer correlated with the concentration of hydrogen, because due to the equilibrium between $\alpha$-Pd–H, i.e. palladium with hydrogen dissolved, and $\beta$-Pd–H, i.e. the hydride phase, the activity of hydrogen, and thus the potential, is pinned [77].

One question that arises is how the pH in the nanoscopic electrolyte layer is defined. Since the decrease of potential with increasing hydrogen amount is in fact caused by the transfer of electrons to the metal, according to $H_{ab} \rightarrow H_{ad} \rightarrow H_{el}^+ + e_{el}$, which occurs as a consequence of the establishment of the thermodynamic equilibrium between $H_{ab}$, $H_{ad}$ and $H_{el}$ of the hydrogen electrode, the concentration of $H_{el}$ in the nanoscopic water layer should change, causing a deviation from the logarithmic behavior. However, logarithmic dependence is observed. Furthermore, when in a double cell set-up with electrochemical cell on one side (entry side) and Kelvin probe on the other side (exit side) is used and a certain potential is applied on the entry side, after a while a corresponding potential is measured also on the exit side by the Kelvin probe. Indeed, a one-to-one relation to the potential at the entry side is observed over a potential range of nearly 400 mV, starting at the low potential side from the binary phase of $\alpha$-Pd–H and $\beta$-Pd–H, indicating that the pH in the water layer does not change significantly [77]. It is suggested that at a potential of 400 mV above the binary phase region the pH in the ultra-thin electrolyte is already very acidic, as the
2.3. How to apply the new detection method for quantitative analysis of hydrogen in materials

With the knowledge of the dependence between the potential measured on the surface of a 100 nm palladium film and the concentration of hydrogen absorbed in it, quantitative measurements of hydrogen are possible. In figure 4 the principle of such measurements was already shown.

In figure 5 it is schematically explained how measurements of permeation of hydrogen through a material and of its presence inside it work. For the case of permeation (see figure 5(a)), the situation is exactly comparable to that of permeation in a Devanathan–Stachurski set-up. First the concentration profile in the sample is established. At the exit side the concentration of hydrogen is kept close to zero. In the Devanathan–Stachurski cell this is achieved by polarizing the exit side to a sufficiently anodic potential so that the hydrogen is oxidized there. Here, due to the low chemical potential of hydrogen in the palladium, the hydrogen goes directly into the palladium film. Thus, finally the same linear gradient of hydrogen activity is established inside the sample, as in the Devanathan–Stachurski technique. The accumulated hydrogen in the palladium is directly comparable to the integrated permeation current, used in the Devanathan–Stachurski method to obtain the time lag, as explained above in figure 1. If a sample already contains hydrogen and then a thin palladium layer is evaporated on its surface, the hydrogen released from the sample will be accumulated inside the palladium (see figure 5(b)). Since release from trap sites is slow, after a while a dynamic equilibrium will be established as explained in figure 5(b) and a nearly constant release rate will be observed.

2.4. Example: measurement of hydrogen in steels

With the calibration reported in [77] it is possible to perform quantified measurements of hydrogen release from steels. An example is shown in figure 6. In that experiment two different kinds of samples, an FeZr model alloy, which was prepared according to Riecke et al [85] and a mild steel sample, both about 1 mm in thickness, were first loaded with hydrogen and then a 100 nm Pd film was evaporated on one side by PVD.

Two sets of samples were investigated: one set was prepared three weeks before the experiment and the other was freshly prepared. As can be seen, for all samples the potential measured on the surface of the 100 nm Pd film decreases with time, due to the uptake of hydrogen from the underlying substrate, with the exception of the palladium film evaporated on a glass slide (which does not release any hydrogen and serves here as a kind of reference). After a while most samples have reached a potential decrease that is linear with the logarithm of time, with the above-mentioned slope of 130 mV per decade (see indicated lines).

**Figure 6.** A Fe–0.23 w% Zr model alloy sample (prepared according to [85]) and a low alloyed mild steel were both loaded with hydrogen for 1 h at −1V_{SH} in 0.1 M NaOH. Then the samples were coated with a 100 nm Pd film and transferred into the Kelvin probe chamber and the change of the work function of the palladium was monitored over time. One set of sample was freshly prepared, the other three weeks before this measurement. One mild steel sample was used in its as-delivered state. After each measurement of about 1000 min, air was introduced into the chamber in order to remove the hydrogen from the Pd. Three consecutive measurements are shown. Release rates are given per cm². Potentials are referenced versus the onset of the binary point (V_{bp}).

The potential of freshly evaporated palladium was usually found much higher and part of the initial decrease in potential after evaporation is due at least partly to the above reaction. Further decrease of potential then does not cause a significant change in pH. This is under further investigation.
Figure 7. Measurement of hydrogen permeation caused by corrosion at the backside of the iron membrane, contaminated by NaCl deposits and exposed to humid air (start of the flow of humid air to the small inner cell at $t = 0$). After about 1000 min a decrease in potential could be observed. At about 3000 min the atmosphere in the small cell was switched to humid nitrogen. The atmosphere in the Kelvin probe chamber was dry nitrogen throughout the experiment. Thickness of the iron membrane was 100 µm, the side facing the Kelvin probe was coated by a 100 nm Pd film. The potential of the Kelvin probe is referred to as $V_{bp}$ i.e. versus the binary phase.

While the slope is an intrinsic property of the palladium film [77], the position of the line provides information about the release rate from the substrate into the palladium film, according to

$$E = E^* - 130 \text{ mV} \times \lg(c) = E^* - 130 \text{ mV} \cdot \lg(jt)$$

In figures 6(a)–(c) three consecutive measurements for about 1000 min each are shown. While at the beginning for most samples higher release rates are measured, after a while lower but constant rates are observed. For the FeZr sample which contains a significant concentration of shallow as well as of deep traps [85], the release rate quickly approaches the release rate of the three-week-old sample, indicating that shallow traps are quickly depleted and that the deep traps are determining the release rate after three weeks.

As the overall release rate will depend on the product of density of traps and the release rate from the traps themselves, according to equation (1) this rate should be $k_{\text{release}} c_T i (1 - n_L) N_L$, it can only remain nearly constant if $c_T$, remains nearly constant, that is if the release rate from the trap sites is very low, as is to be expected from deep traps. The still significant release rate from the FeZr sample is then to be explained with the very high value of $c_T$ [85]. The mild steel sample after three weeks, however, has the same release rate as the as delivered sample, that is all the hydrogen added to the steel by the electrochemical hydrogen loading is lost within three weeks and only very deep trap sites, that are already filled in the as-delivered state remain, leading to the very low but constant hydrogen release rate.

Figure 8. Hydrogen permeation measured by the Kelvin probe method for 100 µm thick iron membranes, loaded on one side with hydrogen at $-0.65 \text{ V}_{\text{SHE}}$ resp. $-1 \text{ V}_{\text{SHE}}$ in unpurged 0.1 M H$_2$SO$_4$. In both cases the binary phase range is quickly reached, by the fast hydrogen uptake into the palladium. In (a) the measured potentials are shown as a function of time. It is difficult to evaluate the saturation permeation current density from these measurements (see dotted lines). In (b) the corresponding concentration of H in the Pd is shown. Here the determination of the time lags according to figure 1 is possible. If the time scale is recalculated by subtracting the time lags, the 130 mV per decade behavior indicating constant rates can be directly seen. Lines: 130 mV per decade.
Figure 9. SKPFM measurement of hydrogen release from a duplex steel sample (composition as stated in [62]) loaded with hydrogen for 1 h at $-1 \text{V}_{\text{SHE}}$ at pH 13 (0.1 M NaOH). The surface was coated by a PVD with a 100 nm thin Pd film directly after hydrogen loading. Then the sample was transferred into the environmental chamber of the SKPFM set-up (dry nitrogen gas atmosphere, $t = 0$). Top row: topography, bottom row: potential (not calibrated). Numbers denote the time passed after introducing into the dry nitrogen atmosphere. The sample surface was etched (see [62]) so that the ferrite grains are topographically lower than the austenite grains. As can be seen, the potential drops faster on the austenite grains. Additionally there are spots of higher hydrogen activity. Over the long measurement times also some lateral diffusion of hydrogen in the palladium layer cannot be excluded, being responsible for at least some of the broadening of the active hydrogen spots or the fading out of not so active areas (see the dashed white circle).

Note the very low hydrogen release rates that can be measured here (7 pA cm$^{-2}$)! This is even more remarkable since the tip area of the Kelvin probe, i.e. the area where the measurement is performed, is less than 0.1 mm$^2$! This example shows how extremely sensitive this new technique is. It also indicates that H$_2$ desorption is negligible on the dry Pd surface!

2.5. Example: measurement of hydrogen permeation

Permeation measurements can be performed with this new method, again with extremely high sensitivity.

Figure 7 shows a measurement where a thin iron membrane ($d = 100 \mu\text{m}$) was mounted in a small cell, as shown in the inset. The surface of the side facing into the...
small cell was contaminated with NaCl. This set-up was introduced into the chamber of the Kelvin probe. The side of the iron membrane facing the Kelvin probe was coated by a palladium film of 100 nm. After equilibration in the dry nitrogen atmosphere, humid air (about 90% r.h.) was purged through the small cell set-up (in the chamber itself the atmosphere remained dry nitrogen), simulating atmospheric corrosion at the contaminated side. After about 1000 min the potential was observed to decrease, with the characteristic 130 mV per decade. At first a permeation current of about 60 pA cm\(^{-2}\) was measured, which then increased to about 100 pA cm\(^{-2}\) after 2000 min. When the atmosphere in the small cell was switched to nitrogen, the permeation rate jumped to 400 pA cm\(^{-2}\), most likely due to the decreased corrosion potential in the nitrogen gas atmosphere.

This example shows how sensitive this method is for permeation studies. And again, the tip area was less than 0.1 mm\(^2\)!

It is highly conceivable that such a sensitive method might be also applicable for cases where low permeation rates over years add to a problem, such as e.g. in thermal solar power plants where over the years even the tiniest hydrogen permeation through the steel receiver tubes gives rise to a serious loss in performance [86].

Also higher permeation rates can be measured, but only for a few minutes, as the palladium film is then quickly filled with hydrogen and the binary phase region of coexisting \(\alpha\)-Pd–H and \(\beta\)-Pd–H then pins the hydrogen activity, which in turn pins the potential measured by the Kelvin probe. An example is presented in figure 8. As can be seen, from the calculated hydrogen concentration in the palladium, based on the calibration reported in [77], the corresponding time lags (as shown in figure 1) can be directly obtained.

Hence, not only very small permeation currents can be measured, that were hitherto not measurable with other techniques such as the Devanathan–Stachurski cell, but also higher permeation currents, although only for a relatively short time. Moreover, as shown in the work by Senöz et al [62] and in figure 3, permeation can also be measured at very high spatial resolution, down to the dimensions of grains and even grain boundaries.

Summarizing, this novel method can be applied for permeation studies just like the Devanathan–Stachurski method, but it provides much higher sensitivity and very high spatial resolution.

2.6. High-resolution studies: use of scanning Kelvin probe force microscopy

Due to its high sensitivity, as discussed, this method can be also applied for measuring hydrogen that is already inside a material. Also this measurement of hydrogen release from materials, as shown in figures 4–6, which is a measure for the real availability of hydrogen in a material, much more relevant than its concentration, can of course be performed with SKPFM at high spatial resolution.

An example is shown in figure 9. As can be seen, the potential decreases faster on the austenite grains. Also some hot spots with very high hydrogen release rates are revealed. It is assumed that these are due to trap sites with very high hydrogen concentration and release rates. Although the measurements are carried out over an extended time (more than 100 h), the contrast is not seriously smeared out by lateral cross diffusion in the palladium film. This is attributed to the fact that the palladium film consists of small nano-grains, i.e. there is a very high density in grain boundaries (which are also suggested to be responsible for the 130 mV per decade dependence of the potential on concentration, instead of the expected 60 mV per decade from the Nernst equation, as discussed above). This high density of grain boundaries in the Pd film, acting as traps, is assumed to significantly inhibit lateral cross diffusion.

This example shows that the application of SKPFM can be a very powerful tool for investigating the interaction of complex materials with hydrogen. However, calibration of the potential scale is difficult to achieve for SKPFM and stable performance over such long times necessary for the study of hydrogen release is also not easy to obtain. Nevertheless, if this technique is combined with additional analytical methods, such as TEM for identifying the nature of the active spots, it may become an important key technique.

Note that some of the active spots in figure 9 do not show a corresponding feature in the topographical map. Hence, most likely the corresponding traps are somewhat below the surface. This unfortunately makes it quite difficult to find exactly the same spot again for further analysis. Nevertheless, this is exactly the procedure necessary for correlating micro-structural features and their activity for hydrogen release, contrary to other techniques that just allow the measurement of the presence of hydrogen at a certain site, such as e.g tritium autoradiography or microcontact printing. Even recent successes of using atom probes for measuring hydrogen at trap sites, with atomic and elemental resolution.
resolution [87, 88] will not readily provide information on the release activity of these trap sites, as it is a destructive method only providing snapshots, although of extreme resolution.

Comparing the results obtained with SKPFM on permeation through duplex steel, as reported in [62], and release from hydrogen-loaded duplex steel, as shown in figure 9, it can be concluded that while for permeation the change in potential is first observed on the ferrite grains [62], the opposite is observed for the hydrogen release from the hydrogen loaded samples. The reason for this is schematically explained in figure 10.

3. Conclusion and outlook

We have presented a novel method, based on Kelvin probe microscopy, which allows the measurement of hydrogen permeation through materials and of its distribution inside materials with unprecedented sensitivity and spatial resolution. Hence, this technique will be of interest for a great number of scientists working on hydrogen-related topics in the wide field of materials science. If measurements are carried out in dependence of temperature an evaluation of trap energies should be possible, again with spatial resolution. This is the object of current research.

While qualitative studies, carried out e.g. with the widespread SKPFM technique, are relatively easy to perform, careful calibration is required, however, before reliable quantification is possible. Evaporated layers of different thickness show different slopes, as the role of grain boundaries and the interface changes with thickness. For 10 nm thick films we observed about 300 mV per decade and for 500 nm thick films about 110 mV per decade. Also differences in the evaporation process itself are expected to cause different dependences. This will make it necessary that, for applications in different labs, calibrations have to be done. Also, humidity plays a role; even slight variations may cause changes in the potential, due to the effect of the ordered water molecules in the ultra-thin water layer on the surface potential. Hence, it is important to keep the humidity at constantly low levels. Of course, the hydrogen electrode also establishes at higher humidity, but it seems to be less stable. Higher rates of Faradaic side reactions, such as reduction of residual oxygen, might play a detrimental role. In general it is expected that the higher the humidity, the closer the electrode will behave to a conventional one. Despite these requirements, which are not trivial to achieve, we believe that this method will have a great impact in a wide application range. As the sensitivity is achieved by accumulating the hydrogen over time, and loss of hydrogen from the palladium obviously is very low, the achievable sensitivity for permeation is assumed to be better than pA cm−2. The sensitivity for releasable hydrogen in steel is well below 0.01 at. ppm.

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