

Spatially resolved high sensitive measurement of hydrogen permeation by scanning Kelvin probe microscopy



S. Evers*, C. Senöz, M. Rohwerder

Christian-Doppler Laboratory for Diffusion and Segregation Phenomena, Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, D-40237 Düsseldorf, Germany

ARTICLE INFO

Article history:

Received 10 January 2013

Received in revised form 23 April 2013

Accepted 27 April 2013

Available online 13 May 2013

Keywords:

Kelvin probe

Hydrogen

Corrosion

ABSTRACT

Recently we have introduced a novel Kelvin probe based approach for spatially highly resolved and highly sensitive measurement of hydrogen in materials and its permeation through materials. In this work we will show how this can be applied for detecting active corrosion sites on the surface of a material from the backside. At the low potentials of actively corroding metal hydrogen uptake occurs at defect sites of the coating and this can be monitored by detecting the resulting higher detectable hydrogen permeation currents at the backside. High lateral resolution is possible in general, however, the achievable resolution is limited by the thickness of the material to be investigated and for longer monitoring times also lateral cross diffusion in the palladium detection layer has to be taken into account.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Hydrogen in metals is a topic of great importance in materials science. It may be desired, such as e.g. for hydrogen storage in metal hydrides [1], or undesired, such as e.g. in high strength steels or other alloys where it may cause hydrogen embrittlement, which is a serious safety and performance problem e.g. in constructions, planes and medical implants [2–7], or e.g. in thermal solar power plants where over the years even tiniest hydrogen permeation through the steel receiver tubes causes of a serious loss in performance [8]. Unfortunately, the existing methods for high sensitivity measurements of hydrogen uptake into, the permeation through and its distribution in metals such as Devanathan–Stachurski cells [9,10], thermo-desorption spectroscopy [4], or hydrogen micro-printing [11] are limited in sensitivity and spatial resolution.

Recently we have introduced a novel approach that utilizes Kelvin probe microscopy for detecting hydrogen [12–15]. This is based on the fact that work functions measured on metals and semiconductors exposed to the environment can be interpreted as electrode potentials [16,17]. When hydrogen uptake occurs on one side of a metal sheet and the hydrogen permeates through the material and reaches the other side of the sheet the hydrogen acts as a reducing agent. For iron oxide, for instance, this results in a partial reduction of Fe^{3+} states in the native iron oxide layer to Fe^{2+} states [12,15], which results in a change of work function and thus can be directly measured by Kelvin probe [12,15].

However, due to the complexity of native oxide layers on steel the resulting potential values are not very reproducible [15] and the response will differ for different kind of steels. Furthermore, the chemical potential of hydrogen in the oxide is higher than in the metal, which would make measurements of permeation currents difficult to perform even if the response was reproducible. This problem can be overcome by applying a thin layer of palladium on the exit side [14,15]. The chemical potential of hydrogen in the palladium is much lower than the one in the steel, i.e. the palladium acts as a drain for hydrogen. Hence, just like in a conventional Devanathan–Stachurski cell, a linear gradient in the hydrogen concentration is established across the sheet [14,15]. The hydrogen that is accumulated in the palladium layer causes a work function change of this layer, that was found to be correlated to the formation of a hydrogen electrode on the surface of the palladium and thus a work function measurement can be directly used to determine the amount of hydrogen accumulated in the palladium layer [14,15]. This way, precise and spatially resolved measurements of hydrogen permeation can be performed. By use of the atomic force microscopy (AFM) based scanning Kelvin probe force microscopy (SKPFM) even differences in the hydrogen permeation through different grains or along grain boundaries can be measured [13,15]. As the palladium acts as very efficient drain even hydrogen bound to trap sites in steels will be accumulated in a palladium layer that is applied on the surface of the steel and differences in the distribution of traps sites can be directly detected [15].

One especially interesting application of this Kelvin probe based approach for measuring hydrogen would be to detect corrosion sites or even differences in local corrosion activity at one side of a component, such e.g. at the inner side of a steel tube, on the other

* Corresponding author. Tel.: +49 2116792510; fax: +49 2116792218.
E-mail address: evers@mpie.de (S. Evers).

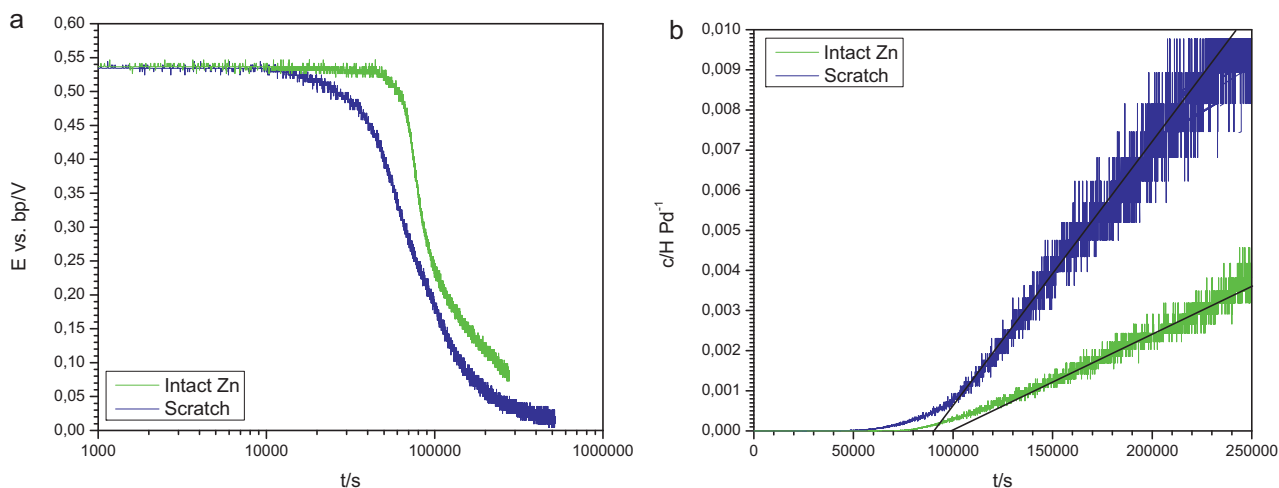


Fig. 1. Evolution of the potential measured at the 100 nm Pd coated back side of the sample exposed to aqueous 0.1 M NaCl electrolyte. Left: original data; right: calculated concentration of hydrogen taken up in the Pd film. Blue curve: data obtained at the scribe, green curve: data obtained with the unscribed sample. After a time lag period a constant permeation current of about 8 nA/cm^2 is obtained for the scribed sample and of about 3 nA/cm^2 for the unscribed sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

side, such as the outer side of the tube. In this case the hydrogen activity established as a consequence of corrosion is used as signal for the corrosion process. This is an application rather for the standard scanning Kelvin probe than for SKPFM, as the possible resolution is expected to be limited by the wall thickness.

It is the aim of this work to evaluate the applicability of the Kelvin probe approach for measuring hydrogen for detecting sites of different activity of corrosion from the back side of a component. One question related to this is whether the low hydrogen activities that can be expected under usual corrosion conditions can be detected, as the correlated permeation currents are to be expected to be extremely low.

The potential values presented here are referenced vs. the onset point of the binary phase (bp) region of palladium containing dissolved hydrogen and palladium hydride [14,15].

2. Experimental

The in-situ Kelvin probe measurements were performed in a custom made set-up, combining an electrochemical cell and a climatic chamber that included the Kelvin probe [15]. The sample is mounted as a membrane between the two cells, with the electrochemical cell on top. This way the upper side forms the working electrode of the electrochemical cell and the bottom side can be monitored by the Kelvin probe tip. This configuration prevents the accumulation of gas bubbles at the surface. The Kelvin probe tip remains in one position, i.e. it cannot be scanned. The KP needle (SS 304) had a diameter of $400 \mu\text{m}$. Low alloyed steel sheet of about 0.8 mm thickness galvanized with about $7 \mu\text{m}$ of zinc was used for the corrosion experiments. 100 nm palladium films were deposited by physical vapor deposition (PVD) in a Leybold Univex 450. The potential maps after the corrosion experiment were performed with a commercially available set-up (Wicinski & Wicinski Surface Scanning Systems, Germany). The KP needle (SS 304) in this Kelvin probe had a diameter of $100 \mu\text{m}$.

For the SKPFM measurements an Agilent 5500 SPM was used for mapping hydrogen release from a thin sheet of duplex steel with coexisting austenite and ferrite phases produced at MPIE (Fe–22.2 wt%Cr–3.7 wt%Ni–1.4 wt%Mn–0.44 wt%Cu–0.31 wt%–0.15 wt%Mo–Si–0.12 wt%N–0.02 wt%C) [13,15]. The duplex steel sample was etched in Behara's reagent (solution of

HCl + distilled water + $\text{K}_2\text{S}_2\text{O}_5$) for 15 s which resulted in the austenitic phase to be less etched than the ferrite phase, making it easy to distinguish the phases in the AFM. Then it was loaded with hydrogen for 1 h at $-1 \text{ V}_{\text{SHE}}$ at pH 13 (0.1 M NaOH). The surface was then coated by 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, $t = 0$).

3. Results

In order to show the high sensitivity of the Kelvin probe approach, a quite challenging task was chosen: corrosion of galvanized steel with a thin scribe of about $100 \mu\text{m}$ width down to the steel. The zinc coating cathodically polarizes the exposed steel surface in the scribe and thus protects the steel from corrosion. The main reaction on the steel surface is oxygen reduction which leads to alkaline pH values directly on the steel surface, where not too high hydrogen activities should prevail. Moreover, under these alkaline conditions the exposed iron will be covered by an oxide layer [18], which will significantly reduce hydrogen uptake at the scribe. Hence, the question that was addressed was whether this small hydrogen uptake could, at least over longer exposure times, lead to detectable amounts of hydrogen. As shown in our earlier works, the Kelvin probe approach for measuring hydrogen by use of a palladium detection layer is very sensitive [14,15]. The thin (100 nm) palladium layer was evaporated on one side of the sample after removing the zinc layer on that side by grinding. On the other side of the sample a defect was prepared by scribing through the zinc layer, exposing the underlying steel. Then the sample was introduced into the electrochemical Kelvin probe set-up, where the other (scribed) side of the sample formed the electrode in a conventional electrochemical cell (entry side). Accordingly, the side pointing towards the Kelvin probe will in the following be denoted as "exit side". The Kelvin probe tip was positioned under the scribe. As a reference another experiment was performed where no scribe was applied, i.e. just homogeneous corrosion of the zinc coating occurred in this case.

As can be seen in Fig. 1 in both cases the potential starts to decrease after some time. Interpreting the measured potentials as hydrogen electrode potentials and using the calibration described

Download English Version:

<https://daneshyari.com/en/article/6615694>

Download Persian Version:

<https://daneshyari.com/article/6615694>

[Daneshyari.com](https://daneshyari.com)