Scanning Kelvin Probe Force Microscopy and electric resistance sensor investigations of hydrogen entry from atmospheric corrosion

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Abstract

Hydrogen embrittlement of advanced high strength steels (AHSS) is an important topic these days. AHSS continues to evolve and grow particularly in automotive industry applications due to desirable mechanical properties. Different aspects of the hydrogen embrittlement phenomenon such as hydrogen entry caused by atmospheric corrosion reactions are currently under intensive research. Two techniques were used for investigation of hydrogen permeation through complex phase (CP) and dual phase (DP) AHSS. Bare and zinc electroplated steel specimens with artificial defects were used. The KircTec sensor is a new device for hydrogen permeation measurements based on monitoring of electric resistance changes. One side of a steel specimen was exposed to wet-dry cycling conditions in a corrosion chamber after application of sodium chloride solution in order to induce atmospheric corrosion, while hydrogen content was measured by the KircTec sensor attached to the opposite side. SKPFM measurements with lateral resolution allowing for identification of permeation paths and the effect of microstructure were conducted using a similar setup. Changes in contact potential difference in controlled atmospheres were monitored in situ after application of a NaCl droplet on the opposite side of an AHSS specimen.

Keywords: hydrogen embrittlement; AHSS; SKPFM

Introduction

In last decades, AHSS grades continue to grow in application especially in automotive industry. These materials were developed in order to fulfil various requirements to body-in-white components as light-weight design for reduction of fuel consumption, improved strength for performance and high formability for production. AHSS are multiphase steels with a fine microstructure, which is different for each AHSS grade leading to different combinations of mechanical properties [1]. For instance, combination of hard martensite phase with soft ferrite phase in different ratio in DP steels allows obtaining a wide range of materials with different strength and formability levels. CP steels have high yield strength and elongation due to a fine and complex ferrite/bainite/martensite microstructure.

However, there is a concern of hydrogen embrittlement (HE) under atmospheric corrosion conditions for steels with high strength level, as atmospheric corrosion is one of the causes of hydrogen entry, which can induce delayed fracture in AHSS [2-5]. Investigation of HE caused by corrosion is an important issue. Available techniques for investigation of HE were described elsewhere [6]. Scanning Kelvin Probe Force Microscopy (SKPFM) was proposed as a promising tool for studying changes of measured contact potential difference (CPD) due to absorbed hydrogen allowing determination of hydrogen distribution with very high spatial resolution [7,8]. A more conventional technique, Scanning Kelvin Probe (SKP), was successfully used for hydrogen permeation detection during hydrogen uptake under atmospheric corrosion after applying NaCl droplet in humid air [9,10]. However, there is a lack of studies investigating hydrogen entry caused by atmospheric corrosion in steels using SKPFM. In this work, the applicability of SKPFM for hydrogen detection during in-situ atmospheric hydrogen loading was assessed.

While SKP and SKPFM may be appropriate techniques for short-term hydrogen detection measurements, there is a need for a tool for long-term hydrogen absorption monitoring. Ootsuka et al. [11] used a system based on the electrochemical permeation technique (EPT) using the Devanathan-Stachurski setup [12] for in-situ monitoring on moving vehicles. They approved applicability of the approach with a temperature-compensation method and found that the amount of absorbed hydrogen changed with the corrosion rate, moving states and chloride loading. Akiyama et al. [13,14] also performed monitoring of hydrogen using a one-half permeation technique during a cyclic corrosion test (CCT). They stated that hydrogen absorption was significantly affected by rust layer formation. In a previous work [15], KircTec sensor based on electric resistance changes due to absorbed hydrogen was compared with the standard EPT. EPT was recommended for laboratory investigations of hydrogen permeability, where high precision is required, while KircTec was proposed as a tool for hydrogen monitoring in real environments. In this work, a KircTec sensor was used for in-situ monitoring of absorbed hydrogen during CCT on bare AHSS and zinc coated AHSS with a scratch.

Experimental

Two grades of AHSS were used in this study: DP1000 and CP1000 with ultimate tensile strength R_m 980 MPa. The microstructure of these steels was described elsewhere [16]. DP1000 contains ferrite, martensite and retained austenite, CP1000 also contains bainite.

SKPFM hydrogen detection is based on findings that absorbed hydrogen changes CPD measured by SKPFM [17]. For SKPFM measurements, DP1000 specimens with dimensions 20×20×0.8 mm were used. Specimens were polished with SiC paper and diamond paste. Two

set-ups (Figure 1) were used for in-situ hydrogen loading during atmospheric corrosion. In the setup a, the side opposite to the side scanned by SKPFM was contaminated with an NaCl aqueous solution droplet in order to observe the evolution of CPD during atmospheric corrosion. In the setup b, NaCl contamination was conducted using NaCl methanol solution, the surface was dried and humidified air at 97 % relative humidity (RH) was blown through a miniature cell attached to the specimen to initiate corrosion.

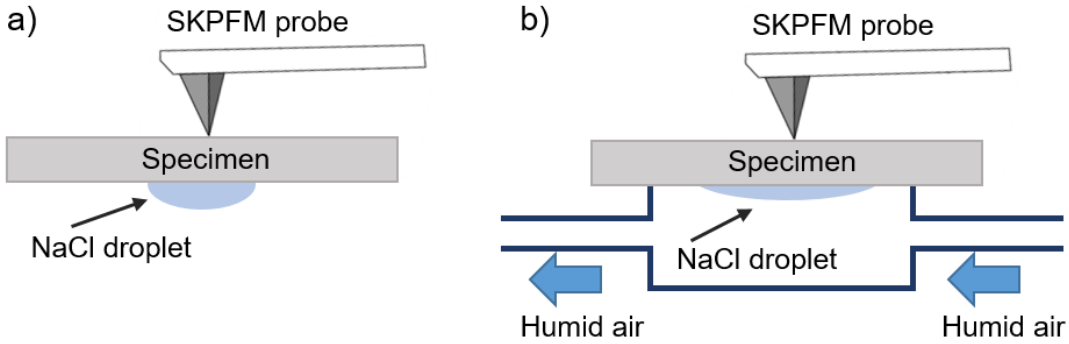

Figure 1: *Schematic drawings of the hydrogen loading during SKPFM measurements; a) by a droplet of aqueous NaCl solution; and b) by NaCl deposits exposed to humid air blowing through the microcell attached to the specimen*

The KircTec device was developed for the measurement of hydrogen diffusion coefficient and for long-term hydrogen monitoring. A KircTec H-probe is made of vanadium alloy with high thermodynamic affinity to hydrogen [18]. Hydrogen diffuses from a steel specimen to an attached H-probe and a KircTec sensor measures diffusible hydrogen by monitoring changes of the electric resistance of the H-probe. For KircTec measurements, two specimens from CP1000 were used: bare specimens and zinc-coated with dimensions 50×50×0.8 mm. A defect with dimensions 0.5×40 mm in the zinc coating down to steel was made. A KircTec H-probe was welded to the steel specimen. In the case of the zinc-coated specimen, a KircTec sensor was welded just below the scratch. The specimen was put into a plastic box with dry air blown through the box to prevent corrosion of steel on the detection side. The opposite side was exposed to CCT (Figure 2). Each 24-hour CCT cycle consisted of dry (50 % RH, 10 hours), wet (85 % RH, 10 hours) and two transition (2 hours) stages. The temperature was kept at 25 °C. NaCl was deposited on the specimen surface at the start of exposure, on the 7^{th}, 28^{th} and 44^{th} day of exposure for the bare specimen and at the start of exposure and on the 17^{th} day of exposure for the zinc-coated specimen by applying NaCl in methanol solution. The chloride concentration deposited on the surface in each step was 1 g/m^2.

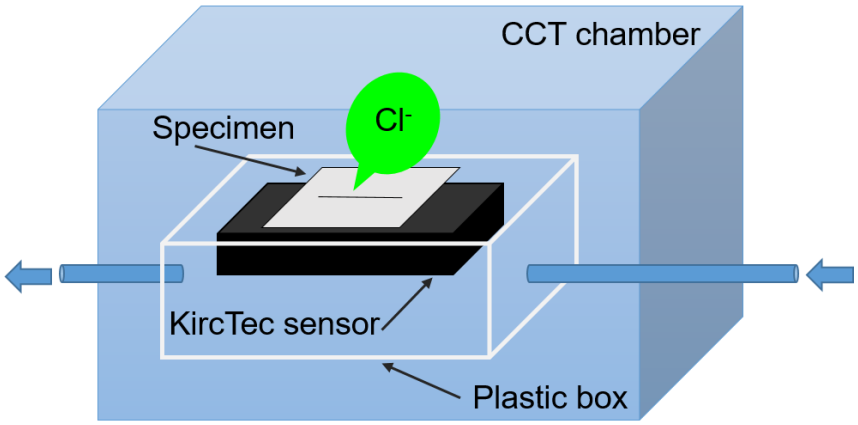

Figure 2: *Schematic drawing of hydrogen absorption monitoring with a KircTec sensor during CCT*

Results and discussion

SKPFM

Results of SKPFM measurements during in-situ hydrogen charging by atmospheric corrosion are presented in Figure 3. In the first experiment, the increase of CPD after applying of NaCl droplet and subsequent fluctuations of CPD values near this higher value were observed. However, a decrease of CPD is expected when hydrogen is introduced into steel [9,10,17,19,20]. Measurements of CPD with a reference Ni specimen before and after the measurement with the steel specimen revealed that CPD changed despite the fact that it should be stable as the Ni surface potential should not change. One of the possible reason is a change of relative humidity in the AFM chamber due to evaporation of the NaCl droplet applied on the opposite side of the steel specimen. Results of an experiment with controlled relative humidity are presented in Figure 3b. In this case, an increase of CPD was observed again, as well as a significant change of CPD measured on the Ni specimen. It indicates that the potential of the AFM tip can change during the experiment and entail specimen CPD changes. It may be caused by contamination or damage of the AFM tip. In Figure 3b, red dots indicate scans with dramatically worsened image quality caused probably by picking up particles from the surface by the AFM tip. Therefore, it needs to be considered carefully if any change of CPD is caused by absorbed hydrogen or it is only a measurement artefact.

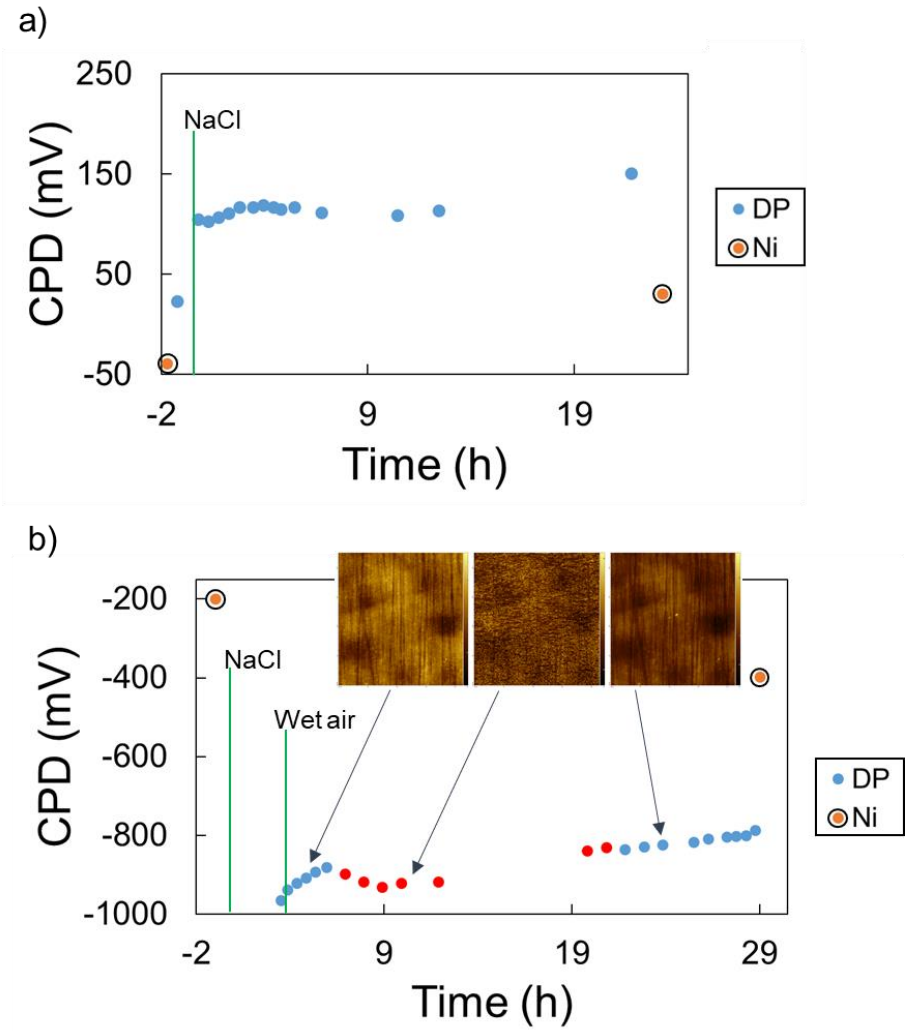

Figure 3: *CPD evolution of DP1000 (DP) and Ni reference (Ni) during SKPFM measurements a) using setup 3a and b) using setup 3b*

SKPFM measurements before and after cathodic polarization of specimen's backside showed results in accordance with other authors [21]. A CPD drop of 300 mV was observed as well as areas with significantly lower CPD values. Similar low-potential areas were observed by Li et al. [19] and Guo et al. [20]. It can be assumed that a high amount of hydrogen produced by cathodic charging overcomes the effect of the changing tip potential. For specimens corroding under atmospheric conditions, a lower amount of hydrogen enters steel, causing smaller changes in CPD. Due to the sensitivity of SKPFM to any minor pollution of the measurement tip, these small changes are easily overlapped with artefacts. This limits the applicability of SKPFM for atmospheric corrosion studies.

KircTec

While SKPFM is able to measure CPD changes caused by hydrogen during a few hours, the KircTec device allows for a continuous measurement of the amount of diffusible hydrogen present in metal for up to months. Results of two long-term measurements are reported in Figure 4. Blue dots shows the maximal hydrogen content in specimens detected during each day cycle. The trend of the increasing hydrogen content during exposure is obvious from the plots. Orange dots are temperature values. KircTec software is able to carry out a temperature compensation procedure, but it can adjust the signal correctly only if the temperature changes

not faster than by 0.2 °C in 2 minutes. Otherwise, temperature changes may influence hydrogen content readings. It can be seen in the plots that the temperature variation affects somewhat the output, but the general trend of the growing hydrogen concentration is still clearly visible.

Repeated contaminations with chloride solution did not influence the increase of hydrogen accumulated in specimens significantly. The measurement with the bare steel specimen was interrupted before the second chloride contamination in order to avoid a temperature jump and a new recording was started after it. It was found to be unnecessary and further contaminations were done without interruptions. It was assumed that the connected strong increase in the hydrogen content may be caused by KircTec software realignment after the measurement interruption and the real diffusible hydrogen content may be lower. For the zinc-coated specimen, the first values of hydrogen content are also doubtful as the hydrogen content reached approximately 0.4 ppm during the first cycle. Based on these observations, it is proposed to compare rates of the hydrogen content growth rather than absolute hydrogen content values. The rate of the hydrogen concentration growth was 0.03 and 0.02 ppm/day between the 2nd and 3rd contamination and between the 3rd and 4th contamination, respectively, for the bare specimen. In the case of the zinc-coated specimen, the rate was 0.07 and 0.03 ppm/day between the 1st and 2nd contamination and after the 2nd contamination, respectively.

These preliminary results suggest that the hydrogen concentration level tends to grow faster initially and than it decreases. It is in accordance with observations of Sakairi et al. [22]. They conducted a CCT exposure with a scratched zinc-coated specimen, where permeating hydrogen was measured electrochemically. The authors supposed that zinc corrosion products may inhibit corrosion and hydrogen generation reactions. This explanation is supported by our observation that the 2nd chloride deposition on the zinc-coated specimen significantly mitigated hydrogen build up.

The results also indicate that the presence of zinc coating with a defect may increase the rate of hydrogen entry into steel. It was also observed by Sakairi et al. that a scratched zinc-coated specimen showed a higher hydrogen permeation current compared to specimens without scratches or specimens with mechanically removed coating [22]. Scharf et al. reported a higher hydrogen uptake in the presence of zinc coating too [23].

The fact that the area of bare steel surface was 80 times smaller for the zinc-coated specimen compared to the uncoated one should be also taken into account. For the non-coated specimen, more homogeneous hydrogen distribution can be assumed as hydrogen uptake can occur on the entire surface of the exposed side, while hydrogen uptake is localized for the coated specimen as hydrogen reduction occurs only on the exposed steel surface [23].

Influence of different CCT phases on hydrogen uptake would also be interesting to evaluate. The corrosion rate measured with iron resistometric probes [24] during the experiments was 4 and 70 μm/year for the dry and wet phase, respectively. Tsuru et al. reported that the hydrogen permeation rate in iron was maximal during the drying [2]. Akiyama et al. reported that hydrogen entry is not directly controlled by corrosion rate and the pH of rust layer was proposed as a factor affecting the hydrogen entry efficiency [13]. Experiments addressing these aspects are currently in progress.

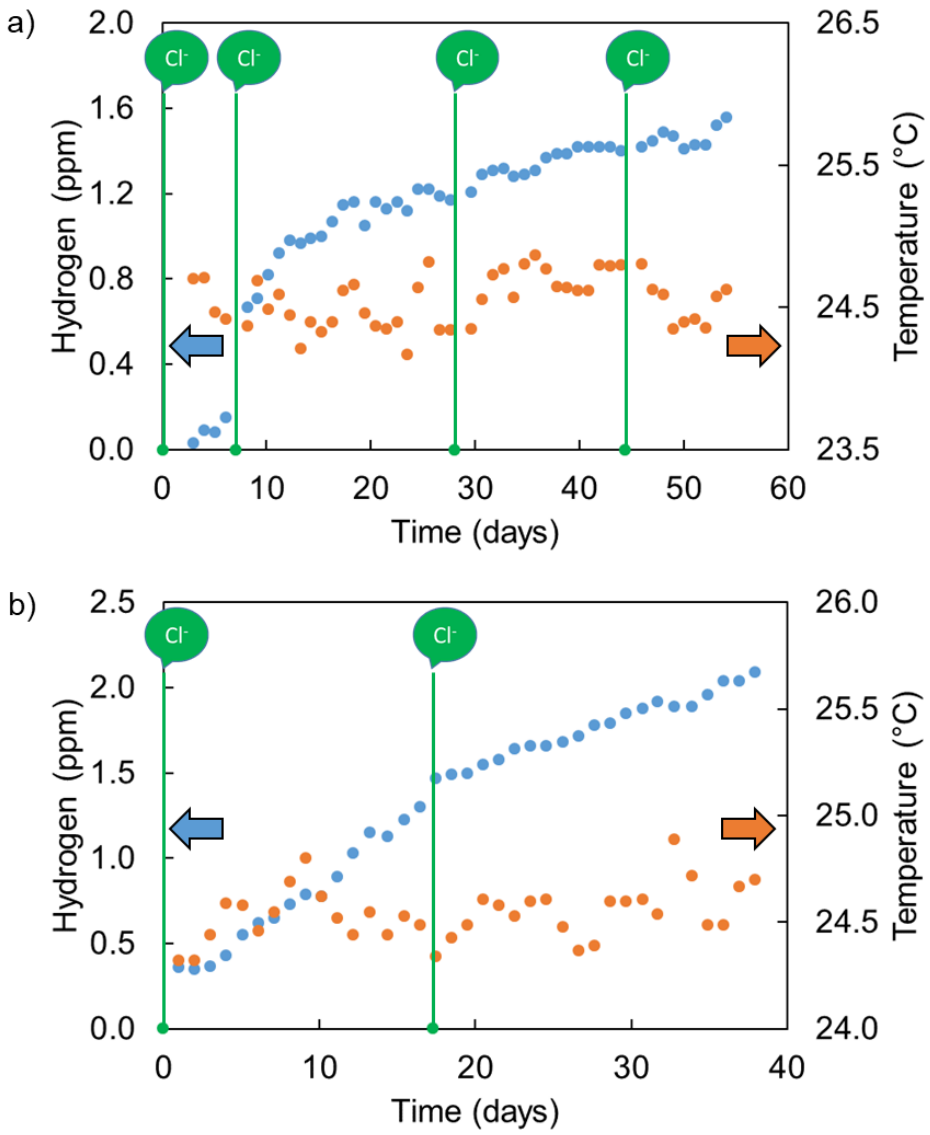

Figure 4: *Evolution of diffusible hydrogen content measured by KircTec sensor on a) bare CP1000 specimen b) zinc-coated CP1000 specimen with a defect in the coating*

Conclusions

1. The applicability of SKPFM for real-time hydrogen entry measurements under atmospheric corrosion conditions is limited due to a low signal-to-noise ratio. The measurement response can easily be overlapped with CPD changes caused by SKPFM tip contamination. However, SKPFM proved to be useful for studies in combination with electrochemical hydrogen charging.
2. Long-term monitoring of diffusible hydrogen uptake in atmospheric environments by the KircTec electric resistance sensor provides promising results. This technique is an interesting alternative to electrochemical detection of hydrogen permeation current.
3. Preliminary results indicated a higher hydrogen uptake in a defect of zinc-coated steel compared to bare steel.
4. The rate of hydrogen content growth decreased with time of exposure for both uncoated and coated specimens.

Acknowledgements

A part of this research was financially supported by the Czech Science Foundation, project No. 17-22586S.

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