

SCANNING KELVIN PROBE STUDY OF HYDROGEN FORMED DURING ATMOSPHERIC CORROSION

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Abstract

One of the intensively studied issues regarding hydrogen embrittlement of advanced high strength steels (AHSS) is the absorption and diffusion of hydrogen produced by atmospheric corrosion. Scanning Kelvin Probe (SKP) is a tool sensitive enough to detect low amounts of hydrogen formed during atmospheric corrosion. In this work, SKP was used to study the effect of the presence of corrosion products on hydrogen uptake and permeation through AHSSs specimens. Corrosion was initiated on one side of the specimen contaminated with a corrosion activator, while Volta potential mapping on the opposite side allowed for in-situ hydrogen detection. Hydrogen release indicated by low potential areas in the maps corresponded to the locations of corrosion products on the opposite side. This shows that hydrogen entry is linked to the presence of red rust.

Keywords: High strength steels, hydrogen, atmospheric corrosion, SKP

1. INTRODUCTION

A topic of great importance in the frame of advanced high strength steels (AHSS) research is their susceptibility to hydrogen embrittlement (HE), as it can be an aspect limiting wider utilization of AHSS in different fields of industry. Detailed study of hydrogen entry caused by atmospheric corrosion is necessary in order to predict the threat of hydrogen-induced degradation during service of any steel structure. It was shown that even very low levels of absorbed hydrogen can lead to the change in the fracture behaviour [1-3]. Any techniques for studying the HE phenomena under atmospheric conditions should be sensitive enough and allow for in-situ hydrogen detection during exposure to a corrosive environment. The principle of the hydrogen detection is often based on the reaction of hydrogen permeating through a sample with species on the detection side. In case of the electrochemical permeation technique, hydrogen is introduced on one side of a steel membrane and after passing the metal is oxidized on the exit side by applying anodic polarization [4]. Evaluation of changes in measured anodic current allows for determination of hydrogen diffusion and trapping characteristics [5,6]. A modified EPT setup was used to study the influence of environmental parameters on hydrogen uptake behaviour, when instead of cathodic polarization on the entry side, corrosion reaction under conditions of cyclic corrosion test or outdoor exposures took place [7-10]. It was demonstrated that hydrogen entry can be influenced not only by the actual climatic parameters of the corrosion process, but also by formation of a layer of iron corrosion products (red rust) and its acidification. It should be taken into account that atmospheric corrosion is spatially very inhomogeneous as well as corrosion products distribution on the metal surface and hydrogen entry can differ from region to region. Techniques allowing for measurements of more localized hydrogen diffusion paths are needed for detailed studies.

The scanning Kelvin probe (SKP) technique fulfils these requirements. It is sensitive to very low hydrogen concentrations and can be used for in-situ studies of localized hydrogen uptake. It maps contact potential difference (CPD) between the reference probe and the sample [11]. Hydrogen detection is based on the decrease of the steel work function when hydrogen permeating through the specimen reduces Fe³⁺ to Fe²⁺ of the native steel oxide layer [12]. Diffusible hydrogen can be quantitatively measured when steel is coated with Pd, as it works like Pd:H electrode even in dry atmosphere [13]. SKP measurement of hydrogen on iron and steel with passive oxide film was shown to provide useful information about hydrogen permeation [14,15]. In the case of SKP, an area large enough to measure both affected and unaffected area can be scanned. Scanning Kelvin probe force microscopy (SKPFM), however, is able to measure only a small area, usually not exceeding 100×100 μm. Thus, it is almost impossible to observe a CPD difference between the region with absorbed hydrogen and the reference surface. However, due to its high spatial resolution, SKPFM was applied to study hydrogen permeation within individual grains and microstructural features [16-20]. Rohwerder and Turcu [21] stated that SKPFM is subject to more artefacts than standard SKP and only the CPD contrast can be meaningful. In our previous study, it was underlined that changes of SKPFM tip potential due to tapping at the surface should be also taken into account as it can influence measured CPD, especially when concentration of hydrogen is very low [22]. For in-situ studies, detection of hydrogen entered into steel during corrosion with SKP seems thus preferable.

In this work, experiments with SKP were carried out in order to measure the hydrogen release at the exit side of steel specimens, while hydrogen was introduced into the specimens due to atmospheric corrosion on the opposite side. The effect of the presence of corrosion products on the entry side on the hydrogen uptake was evaluated.

2. EXPERIMENTAL

Complex phase steel CP1000 with ultimate tensile strength Rm 980 MPa was used for the measurements. The chemical composition of the steel is given in **Table 1**. Sheet specimens of 0.8 mm thickness were mechanically polished. Pre-corroded entry surfaces were prepared by exposing specimens to two 24-hour cycles according to EN ISO 3231. Each cycle consisted of 8-hour exposure to air at 100 % relative humidity (RH) with addition of 0.2 l SO₂ to 300-l climatic chamber maintained at 40 °C and 16-hour exposure to air at 23 ± 5 °C and 50 ± 20 % RH. The hydrogen detection (exit) side was isolated with tape during the pre-exposure to prevent corrosion. After formation of a red rust layer, specimens were annealed at 200 °C for 2 hours in order to remove any absorbed hydrogen.

Both the pre-corroded and reference freshly polished specimens were exposed to air at 55 % RH for 24 hours in order to produce stable and reproducible oxide layer on the exit side surface.

Table 1 Chemical composition of CP1000 AHSS; maximal contents of alloying elements given in wt.%

Material	C	Si	Mn	P	S	Al	Cr+Mo	Nb+Ti	V	B
CP1000	0.23	1	2.7	0.08	0.015	1.4	1	0.15	0.2	0.005

After measuring the initial CPD, the entry side of the specimens was contaminated with NaCl solution to obtain the surface chloride concentration of 10 μg/cm², approximately. The CPD mapping of the opposite (exit) specimen side was performed using SKP from Wicinski & Wicinski GbR with Ni probe of 170 μm diameter. The experiments were carried out in the atmosphere of controlled RH of 85-90 % ensuring corrosion reaction on the hydrogen absorption side. Potential of the SKP tip was calibrated using Cu crucible filled with saturated CuSO₄ solution and CPD was recorded against standard hydrogen electrode. Repeated scans were carried out in order to investigate evolution of CPD in time.

3. RESULTS AND DISCUSSION

SKP scans were performed on the side opposite to the side contaminated with NaCl and exposed to humid air. In **Figure 1**, the evolution of CPD maps during the corrosion process is shown. The area corresponding to the contaminated zone is indicated by dotted lines. CPD distribution maps of a specimen without red rust layer on the back (**Figures 1a-c**) illustrate that the CPD distribution was quite homogeneous shortly after the contamination. It started to decrease at the left hand side of the contaminated area a few hours later. In case of the pre-corroded specimen (**Figures 1d-f**), a CPD drop was observed already in the first measurement only 2 hours after the contamination. It is known that hydrogen diffusion coefficient in CP1000 is quite high [23] and the time lag for the first specimen can thus be attributed to the time needed for red rust formation. In contrary, the pre-corroded specimen was already covered with corrosion products and the hydrogen entry process could start immediately after the contamination. The expansion of the low CPD area can be related to the lateral diffusion of hydrogen in the steel, which was reported elsewhere [15].

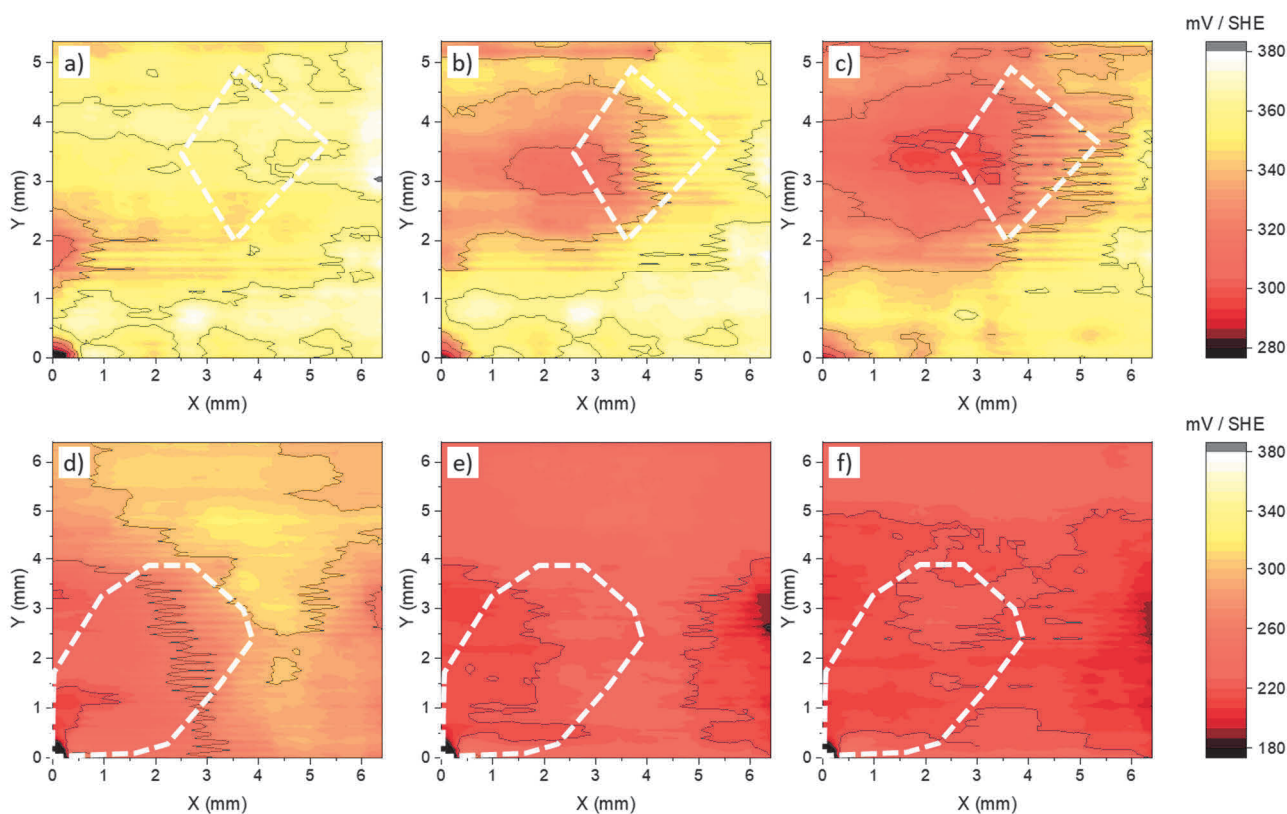


Figure 1 CPD maps measured during atmospheric corrosion of the opposite side for a specimen without red rust layer after a) 2 hours, b) 21 hours and c) 42 hours after contamination with corrosion activator and for a pre-corroded specimen after d) 2 hours, e) 6 hours and f) 29 hours after contamination

Figure 2a indicates that the area of lower CPD corresponds to the region of red rust formation and there is no significant CPD decrease in the contaminated area without corrosion products. For the pre-corroded specimen in the **Figure 2b**, the low CPD area correlates with the contaminated area.

The evolution of CPD in time is presented in plots in **Figure 3**. Plotted data are the average values of CPD for two selected lines inside the contaminated area and in the reference area. CPD before the contamination was slightly lower than CPD of the reference area during the first measurement indicating possible oxidation of the detection side. The problem with the stability of the potential on the detecting side can be solved in the future

by using Pd coating [24]. For the fresh specimen, a decrease of CPD occurred 7 hours after the contamination and the total CPD drop of the contaminated area versus reference area was 50 mV. In contrast, the total CPD drop measured on the pre-corroded specimen was 120 mV. The significant decrease of CPD at the contaminated area appeared rapidly and it was detected already during the first measurement. Only a slight further decrease was observed. It is also obvious that CPD of the reference area decreased as well but with a lower rate and achieved near the same value of CPD at the end of the exposure. It can be assigned not only to the lateral diffusion, but also to possible other hydrogen entry sites due to the presence of the red rust layer.

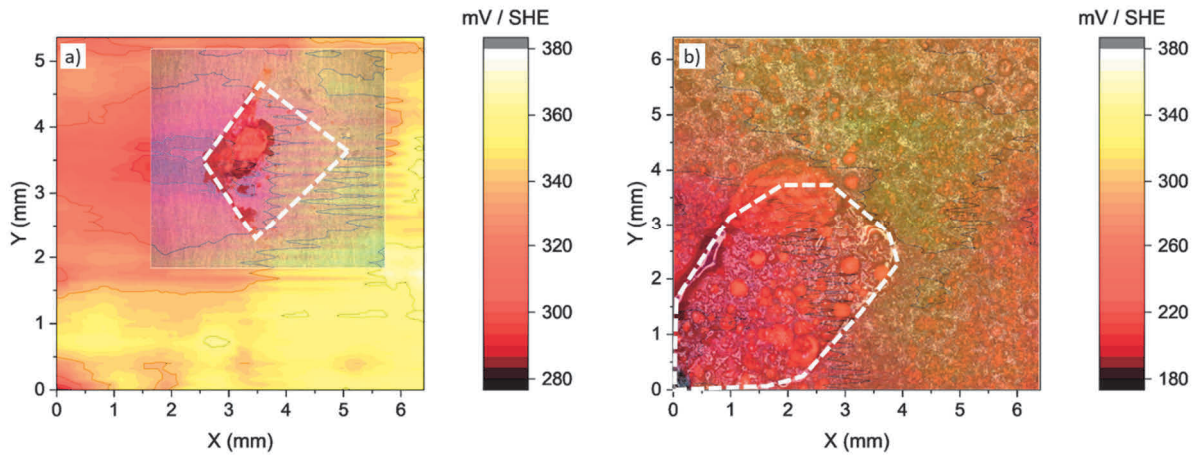


Figure 2 Overlaid CPD maps and micrographs of the opposite side of specimens a) with fresh surface and b) pre-corroded surface after 42 hours and 2 h of exposure to humid air

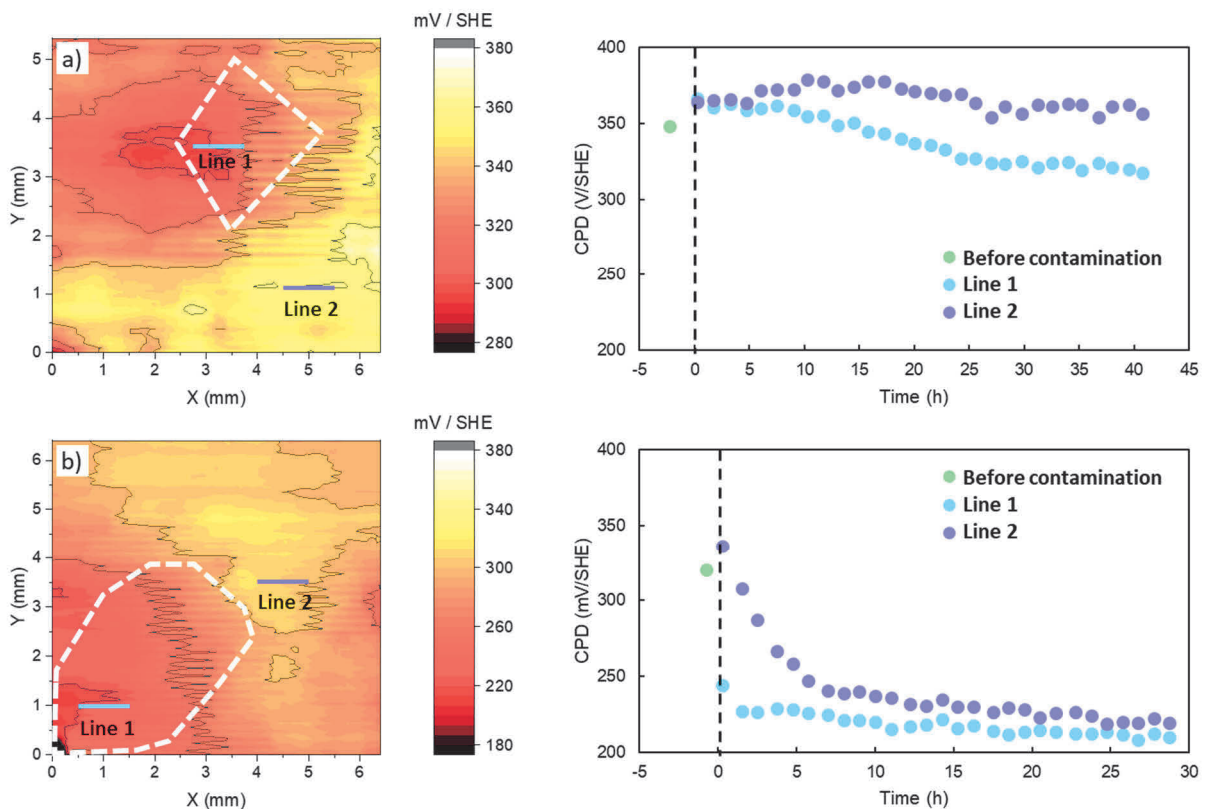


Figure 3 Evolution of average CPD for selected lines measured on the opposite side of the specimen a) with fresh surface and b) with pre-corroded surface

These observations confirm the major role of the presence of corrosion products on hydrogen entry. It is in accordance with previous works suggesting that red rust formed on steel causes a drop in pH, which enables enhanced hydrogen uptake into steel [7,25]. It should also be noted that red rust present on the pre-corroded specimen contains sulphates which were reported to further contribute to the pH drop and able to enhance hydrogen uptake [26].

4. CONCLUSIONS

SKP was used for in-situ hydrogen detection during atmospheric corrosion. CPD measurements carried out on a pre-corroded specimen and on a specimen without red rust indicate that the process of hydrogen uptake is linked to the presence of corrosion products. Presence and possibly the chemical nature of iron corrosion products (red rust) can significantly enhance hydrogen entry.

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