

HYDROGEN DETECTION IN HIGH STRENGTH STEELS BY MEANS OF SKPFM

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Abstract

Growing efforts for weight and gas emission reduction in automotive industry led to development of advanced high strength steels (AHSS) with a very good strength-to-ductility balance. However, AHSS can be prone to hydrogen embrittlement, which leads to the degradation of mechanical properties, mainly ductility, in the presence of hydrogen. It can limit the applicability of AHSS for the car body construction. Therefore, it is crucial to assess the risks associated with hydrogen absorption in AHSS during corrosion processes.

In this work, a novel technique for hydrogen detection was used. Scanning Kelvin probe force microscopy (SKPFM) enables measurement of Volta potential difference with very high spatial resolution. SKPFM measurements of changes in Volta potential difference were performed on an AHSS grade in order to study hydrogen entry and absorption as a result of atmospheric corrosion and electrochemical hydrogen charging.

Keywords: High strength steels, hydrogen, SKPFM

1. INTRODUCTION

Hydrogen embrittlement (HE) of steels is a relatively well-known phenomenon. In recent years, the growing interest in investigation of HE of AHSS reflects a lack of information about the HE mechanism and interaction between the AHSS microstructure and hydrogen and also the increasing demand for wider utilization of AHSS in automotive industry. There are still many questions concerning the effect of hydrogen generated during atmospheric corrosion as hydrogen induced by this source may cause unexpected failure of AHSS components [1-3].

A number of techniques are known to be useful for studying HE of steels such as slow strain rate testing, electrochemical permeation technique, hydrogen microprint technique, thermal desorption spectroscopy etc. [4,5]. These modified techniques may be suitable for study effect of hydrogen absorbed during atmospheric corrosion, but techniques with higher sensitivity and better spatial resolution are needed for study of HE in view of steel microstructure. They are limited in sensitivity and spatial resolution. Scanning Kelvin Probe (SKP) and Scanning Kelvin Probe Force Microscopy (SKPFM) were shown to be a useful tool to provide information on the release of hydrogen from metal samples. It is based on that the hydrogen can be absorbed on one side of the metal, permeates through the sample and changes the Fe^{3+} / Fe^{2+} ratio by reduction of Fe^{3+} species on the opposite side which leads to decrease of Volta potential measured by SKP [6]. In the case of Pd-coated samples, diffusible hydrogen leaves the sample, accumulates in a Pd layer and the amount of hydrogen may be calculated from measured Volta potential as there is logarithmical correlation between them [7]. SKP

technique was successfully applied for hydrogen detection after electrochemical hydrogen charging [8-10], during in-situ charging [11-13] and during atmospheric corrosion [8,14].

SKPFM is a mode of Atomic Force Microscope (AFM). After topography mapping of one line, the AFM cantilever is lifted and Volta potential difference is measured from electrical excitation of cantilever applying the voltage to the tip. The principle of hydrogen detection is the same as using standard SKP. Detail comparison of the techniques is given elsewhere [15]. While SKP provides micro- and even sub micro-scale resolution, SKPFM enables Volta potential mapping with spatial resolution in a range of nanometers due to very small size of the probe tip. Due to this fact, SKPFM seems to be promising technique for studying hydrogen permeation in AHSS with very fine-grained microstructure. On the other hand, Rohwerder and Turcu [15] underlined a number of possible artefacts, which should be taken into account for correct interpretation of results. Although SKPFM measurements were performed on duplex steels after hydrogen charging [13,16-18], the use of this technique for detection of hydrogen formed under atmospheric corrosion conditions was not reported up to now.

It is the aim of this work to study the applicability of SKPFM for detection of hydrogen produced from atmospheric corrosion in AHSS. Changes in Volta potential caused by hydrogen associated with local microstructure features would bring valuable information about distribution of hydrogen in AHSS and its permeation paths.

2. EXPERIMENTAL

The AHSS used in this work was DP1000, dual phase steel with ultimate tensile strength Rm 980 MPa. The chemical composition of the steel is shown in **Table 1**. The microstructure of the steel was described elsewhere [19]. DP1000 contains martensite, ferrite and retained austenite. SKPFM measurements were performed on samples with dimension 20 mm × 20 mm × 0.8 mm. One side of the specimens was polished with SiC paper to 1200 grit, the opposite side was polished with SiC paper to 4000 grit and then with diamond paste. Specimens were degreased with ethanol and dried. Pure nickel obtained from Goodfellow Cambridge with purity over 99.99 % was used as a reference material. The Ni sample was prepared by polishing with SiC paper and diamond paste, degreasing and drying.

Table 1 Chemical composition of DP1000 AHSS; maximal contents of alloying elements are given in wt. %

Material	C	Si	Mn	P	S	Al	Cr+Mo	Nb+Ti	V	B
DP1000	0.18	0.8	2.5	0.08	0.015	2.0	1.4	0.15	0.2	0.005

Three setups were used in order to introduce the hydrogen into steel specimens. The setups are schematically illustrated in **Figure 1**. In the setup a, one side of the specimen, polished to 1200 grit, was cathodically polarized and the opposite side was measured by SKPFM before and after charging. The charging was carried out in 0.5 M H₂SO₄ aqueous solution with addition of 40 mg / l thiourea as a recombination poison. The charging current density was 10 mA / cm² and the time of charging was 40 minutes. In the setup b, the side opposite to the side scanned by SKPFM was contaminated with NaCl aqueous solution droplet without drying in order to observe the evolution of Volta potential difference during atmospheric corrosion. This setup was modified to the setup c, where NaCl contamination was performed using NaCl methanol solution, the surface was dried and humidified air at 97 % relative humidity was then blown through a miniature cell attached to the specimen to initiate corrosion.

AFM AIST-NT SmartSPM 1000 was used for the SKPFM measurements. The probes in SKPFM measurements were ElectriTap190-G tips with Cr/Pt conductive coating with a force constant of 48 N / m and a resonant frequency of 190 kHz.

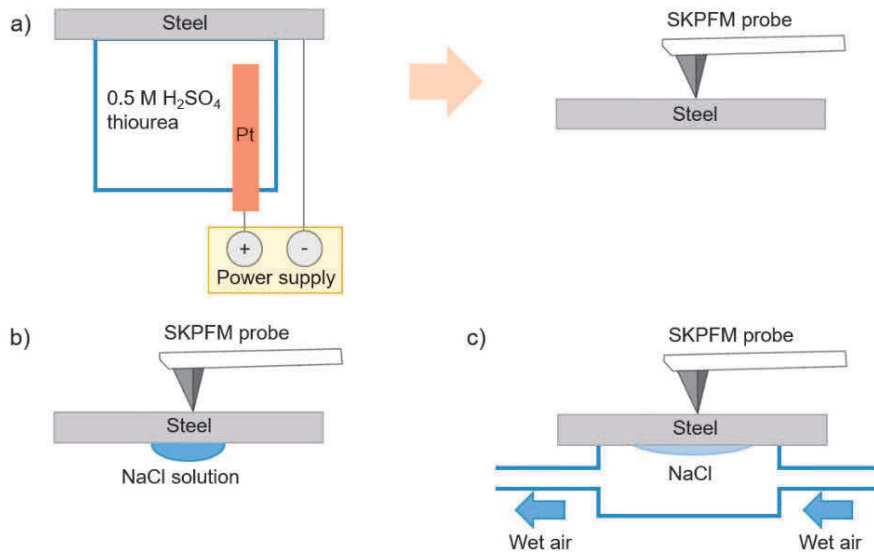


Figure 1 Schematic drawings of the hydrogen charging a) by cathodic hydrogen charging prior to SKPFM measurement b) droplet of aqueous NaCl solution c) microcell with wet air blowing beneath the sample surface contaminated with NaCl methanol solution

3. RESULTS AND DISCUSSION

Using the setup a (**Figure 2**), hydrogen was produced by cathodic polarization on the specimen side opposite to the side scanned by SKPFM. **Figure 2** shows the topography and Volta potential (CPD) maps of the specimen before and after cathodic hydrogen charging measured within the same area as proved by topography scans. Hydrogen charging resulted in the Volta potential drop of 300 mV. It is in accordance with results of Senöz et al. [16]. Areas with more negative potential are visible on the CPD map after the charging. The difference between areas with higher and lower CPD is approximately 60 mV, whereas Volta potential of uncharged specimen is relatively homogeneous with only 20 mV difference. Li et al. [17] and Guo et al [18] observed low-potential areas at the ferrite/austenite boundaries and inside of ferrite and austenite grains in SKPFM measurements on duplex steel after electrochemical charging. In the present study, the specimen was not etched in order to avoid topography-induced artefacts on the CPD image. Microstructure investigations of the measured area will be carried out for future measurements in order to fit low-potential areas with microstructure features of studied samples.

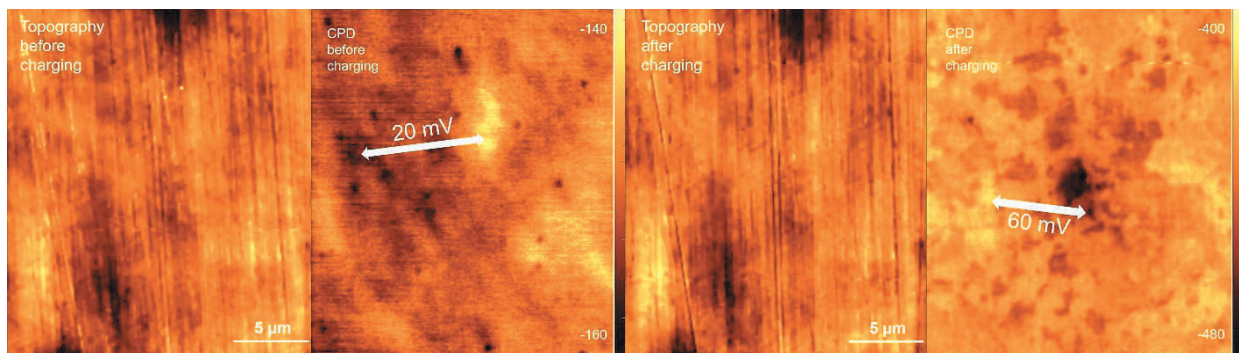


Figure 2 Topography and Volta potential maps before and after cathodic charging with setup 1a

In further experiments, atomic hydrogen is assumed to be formed by atmospheric corrosion of DP1000. Atmospheric corrosion is expected to generate hydrogen that would permeate through the specimen and can be detected on the opposite side by SKPFM. In this case, only a small amount of hydrogen permeating through

the steel was expected. Still, even such small amounts are detectable by SKP as shown by Nazarov et al. [8]. They observed 200 mV potential fall after corrosion of iron in NaCl solution for 24 hours. After 1 week of conditioning in laboratory air the potential drop decreased to 150 mV. It is obvious from **Figure 3a** that CPD of DP1000 was lower before contamination of a specimen with NaCl droplet than after application of NaCl solution. However, the reason of the CPD increase as well as subsequent evolution of CPD is controversial. Already after 15 minutes after NaCl contamination 80 mV CPD jump was detected. It is unlikely to be caused by permeating hydrogen. It was observed by other authors [8,14,16-18] that hydrogen release causes a drop in CPD and not an increase. The stability of the SKPFM probe tip potential was questioned as the CPD is the difference in potentials of a tip and a specimen surface [15]. Any damage or contamination of a probe tip may cause a change of the tip potential and lead to incorrect results. The CPD measurements of pure inert Ni sample before and after a set of CPD measurements with DP1000 were thus conducted. As the potential of Ni is assumed to be stable, the measured CPD should be the same. However, **Figure 3a** shows that the CPD measured for Ni changed by 70 mV. It indicates that the measured changes of CPD for DP1000 could be due to unstable tip potential rather than due to hydrogen release.

The drawback of the setup b is that the relative humidity in the AFM chamber may change because of the NaCl droplet evaporation and humidity changes may influence CPD values [19]. In order to avoid this problem, setup c was used, where blowing wet air through the microcell promotes corrosion reaction whereas the relative humidity in the AFM chamber stay unchanged. Results of these measurements are presented in **Figure 3b**. During this set of measurements, significant contamination or damage of the tip was observed from topography scans. Red colored dots indicate measurements where quality of scans dramatically worsened. It took another 15 hours until the quality of topography scans improved again. In this case, CPD measured with Ni decreased. That confirms that the tip potential was unstable and the observed increase in CPD may be rather an artefact.

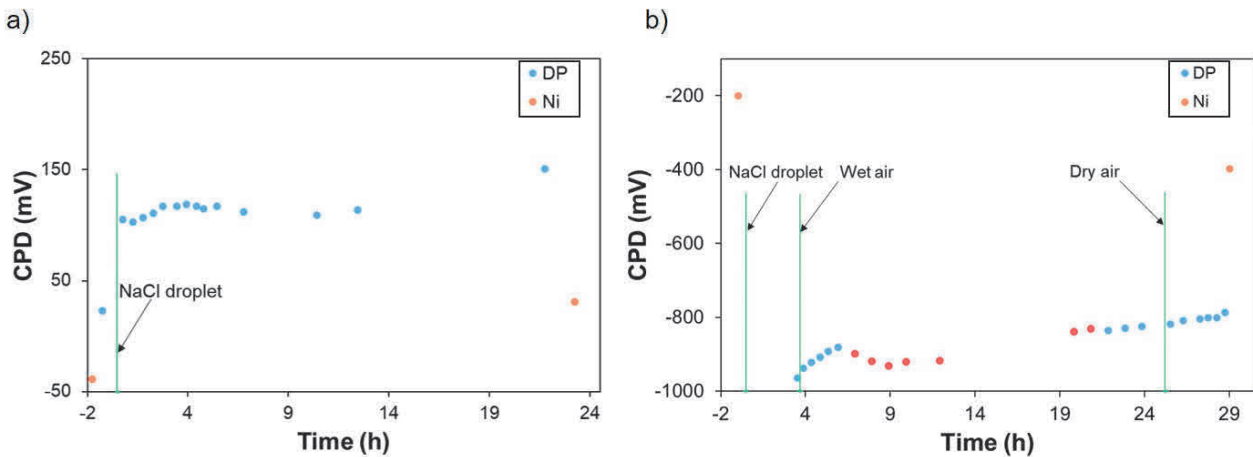


Figure 3 Volta potential evolution a) using setup b and b) using setup c

Obtained results demonstrated that it may be difficult to measure the evolution of Volta potential correctly due to a number of parameters influencing CPD, especially if hydrogen is formed by atmospheric corrosion. Cook et al. [20] suggest SKPFM calibration with a standard SKP, but the effect of tip potential change is still possible and should be taken into account. The use of electrochemical hydrogen charging may be recommended as the amount of formed hydrogen is much higher and the change of CPD induced by the hydrogen release may overcome any influence of changing tip potential. The change of Volta potential difference measured by a standard SKP may bring more correct results as the probe do not touch the surface. Due to the fact that AHSS have very fine microstructures and studying of CPD changing in individual grains or grain boundaries is of high interest, SKPFM still remains a promising technique.

4. CONCLUSION

SKPFM measurements were performed on DP1000 specimens after cathodic charging and during atmospheric corrosion. A 300 mV drop of CPD was observed on the opposite side of a cathodically charged specimen. CPD measurements during atmospheric corrosion showed that the contribution of potential changes of an SKPFM tip may significantly affect the CPD. The standard SKP is recommended as a tool for detection of hydrogen formed in atmospheric corrosion, while SKPFM may be useful for studying CPD changes in a microscale during in-situ hydrogen charging.

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REFERENCES

- [1] AKIYAMA, E., MATSUKADO, K., WANG, M., TSUZAKI, K. Evaluation of hydrogen entry into high strength steel under atmospheric corrosion. *Corrosion Science*, 2010, vol. 52, no. 9, pp. 2758-2765.
- [2] AKIYAMA, E., LI, S., SHINOHARA, T., ZHANG, Z., TSUZAKI, K. Hydrogen entry into Fe and high strength steels under simulated atmospheric corrosion. *Electrochimica Acta*, 2011, vol. 56, no. 4, pp. 1799-1805.
- [3] AKIYAMA, E., WANG, M., LI, S., ZHANG, Z., KIMURA, Y., UNO, N., TSUZAKI, K. Studies of evaluation of hydrogen embrittlement property of high-strength steels with consideration of the effect of atmospheric corrosion. *Metallurgical and Materials Transactions A*, 2013, vol. 44 no. 3, pp. 1290-1300.
- [4] KOYAMA, M., ROHWERDER, M., TASAN, C. C., BASHIR, A., AKIYAMA, E., TAKAI, K., TSUZAKI, K. Recent progress in microstructural hydrogen mapping in steels: quantification, kinetic analysis, and multi-scale characterisation. *Materials Science and Technology*, 2017, vol. 33, no. 13, pp. 1481-1496.
- [5] RUDOMILOVA, D., PROŠEK, T., LUCKENEDER, G. Techniques for investigation of hydrogen embrittlement of advanced high strength steels. *Corrosion Reviews* [online]. 2018. pp. - [viewed 2018-04-15]. Available from: DOI: 10.1515/correv-2017-0106.
- [6] EVERS, S., SENÖZ, C., ROHWERDER, M. Hydrogen detection in metals: a review and introduction of a Kelvin probe approach. *Science and Technology of Advanced Materials*, 2013, vol. 14 no. 1, pp. 014201.
- [7] EVERS, S., ROHWERDER, M. The hydrogen electrode in the "dry": a Kelvin probe approach to measuring hydrogen in metals. *Electrochemistry Communications*, 2012, vol. 24, pp. 85-88.
- [8] NAZAROV, A. P., MARSHAKOV, A. I., RYBKINA, A. A. Iron hydrogenation under atmospheric corrosion. Studies using a scanning vibrating microscope. *Protection of Metals and Physical Chemistry of Surfaces*, 2015, vol. 51, no. 3, pp. 347-359.
- [9] SCHALLER, R. F., SCULLY, J. R. Measurement of effective hydrogen diffusivity using the Scanning Kelvin Probe. *Electrochemistry Communications*, 2014, vol. 40, pp. 42-44.
- [10] WILLIAMS, G., MCMURRAY, H. N. and NEWMAN, R. C. Surface oxide reduction by hydrogen permeation through iron foil detected using a scanning Kelvin probe. *Electrochemistry Communications*, 2013, vol. 27, pp. 144-147.
- [11] SCHIMO, G., BURGSTALLER, W., HASSEL, A. W. Rolling Direction Dependent Diffusion Coefficients of Hydrogen in Ferritic Steel by SDCM Charging and SKP Probing. *ISIJ International*, 2016, vol. 56, no. 3, pp. 487-491.
- [12] SCHIMO, G., BURGSTALLER, W., HASSEL, A. W. Potentiodynamic hydrogen permeation on Palladium-Kelvin probe compared to 3D printed microelectrochemical cell. *Electrochemistry Communications*, 2015, vol. 60, pp. 208-211.
- [13] EVERS, S., SENÖZ, C., ROHWERDER, M. Spatially resolved high sensitive measurement of hydrogen permeation by scanning Kelvin probe microscopy. *Electrochimica Acta*, 2013, vol. 110, pp. 534-538.
- [14] NAZAROV, A., VUCKO, F., Thierry, D. Scanning Kelvin Probe for detection of the hydrogen induced by atmospheric corrosion of ultra-high strength steel. *Electrochimica Acta*, 2016, vol. 216, pp. 130-139.

- [15] ROHWERDER, M., TURCU, F. High-resolution Kelvin probe microscopy in corrosion science: scanning Kelvin probe force microscopy (SKPFM) versus classical scanning Kelvin probe (SKP). *Electrochimica Acta*, 2007, vol. 53, no. 2, pp. 290-299.
- [16] SENÖZ, C., EVERS, S., STRATMANN, M., ROHWERDER, M. Scanning Kelvin probe as a highly sensitive tool for detecting hydrogen permeation with high local resolution. *Electrochemistry Communications*, 2011, vol. 13, no. 12, pp. 1542-1545.
- [17] LI, M., GUO, L. Q., QIAO, L. J., BAI, Y. The mechanism of hydrogen-induced pitting corrosion in duplex stainless steel studied by SKPFM. *Corrosion Science*, 2012, vol. 60, pp. 76-81.
- [18] GUO, L. Q., BAI, Y., XU, B. Z., PAN, W., LI, J. X., QIAO, L. J. Effect of hydrogen on pitting susceptibility of 2507 duplex stainless steel. *Corrosion Science*, 2013, vol. 70, pp. 140-144.
- [19] ÖRNEK, C., LIU, M., PAN, J., JIN, Y., LEYGRAF, C. Volta Potential Evolution of Intermetallics in Aluminum Alloy Microstructure Under Thin Aqueous Adlayers: A combined DFT and Experimental Study. *Topics in Catalysis* [online]. 2018. pp. 1-14 [viewed 2018-04-20]. Available from: DOI: 10.1007/s1124.
- [20] COOK, A. B., BARRETT, Z., LYON, S. B., MCMURRAY, H. N., WALTON, J., WILLIAMS, G. Calibration of the scanning Kelvin probe force microscope under controlled environmental conditions. *Electrochimica Acta*, 2012, vol. 66, pp. 100-105.