



Short communication

Spatial determination of diffusible hydrogen concentrations proximate to pits in a Fe–Cr–Ni–Mo steel using the Scanning Kelvin Probe



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ABSTRACT

The diffusible hydrogen concentration ($C_{H,diff}$) was mapped spatially, proximate to acidic corrosion pits formed in $MgCl_2$ droplets, on an ultra-high strength stainless steel using a Scanning Kelvin Probe (SKP). A secondary hardened martensitic stainless steel (Fe–11Ni–12Cr–1Mo–0.005C–0.02Mn wt%) was evaluated. Predetermined, uniform $C_{H,diff}$ levels quantified by electrochemical extraction after homogeneous cathodic charging, were calibrated versus the SKP potential at 57% RH (0.16 kPa H_2O , 20.26 kPa O_2 , 79.03 kPa N_2 , and 0.55 kPa residual gas species) [1]. Calibration enabled estimation of $C_{H,diff}$ near pitted surfaces. Cross-sections of corrosion damage sites after pitting were also examined to determine the distribution of the $C_{H,diff}$ perpendicular to the exposure surface.

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1. Introduction

Determination of hydrogen uptake in ultra-high-strength steels (UHSS) exposed to severe atmospheric environments is of significant interest given the increasing demand for higher strength materials in aggressive environments. In UHSS under atmospheric exposure, acidic pits formed by the breakdown of the passive film, metal dissolution, hydrolysis, and acidification mechanism are prone to local H production and uptake [2]. This is a critical issue in many applications ranging from automotive to dry cask storage of nuclear waste [3,4]. Determination of such local uptake and concentration mapping is challenging on small length scales.

Hydrogen uptake has been well quantified in many full immersion environments at meso-length scales [5–8]. Techniques for spatial detection at the sub-mm length scales, specifically with lateral detection, are lacking. Tritium autoradiography, nuclear reaction analysis, scanning electrochemical microscopy, microprinting, and rescaled pits using thermal desorption spectroscopy (TDS) were applied for spatial H detection [9–17]. Permeation was employed for temporal resolution of H during atmospheric exposure [18]. The Scanning Kelvin Probe (SKP), SKP force microscope (SKPFM), and SKP combined with TDS and secondary ion mass spectrometry are promising new methods for spatial H detection with lateral and depth profiling (utilizing cross-sections of samples) [19–29]. Recently, the SKP has detected H uptake utilizing a modified permeation technique during atmospheric corrosion [30]. However, these methods have not provided quantification of the local H concentration at confined corrosion sites due to atmospheric uptake.

The objective here was to utilize the SKP on previously corroded surfaces to map diffusible H concentrations ($C_{H,diff}$), consisting of lattice and reversibly trapped hydrogen, associated with local corrosion cells without use of a Pd film on a permeation type exit surface to facilitate detection. Following calibration of the SKP potential (Φ) as a function of $C_{H,diff}$, the SKP was used for lateral H detection across pre-exposed pitted areas. Depth detection was achieved using cross-sectioned, pre-exposed samples.

1.1. Materials and methods

1.1.1. SKP calibration as a function of $C_{H,diff}$

UNS S46500 (Fe–11Ni–12Cr–1Mo–0.005C–0.02Mn (wt%)) in the as annealed/cold-treated condition and H900 temper was evaluated [31]. This steel possesses slow effective hydrogen diffusivity ($D_{H,eff}$) ranging from 3.1 to 6.2×10^{-9} cm^2/s and low uniform corrosion rates [23,32]. This enables SKP mapping without substantial H outgassing before line scans and broad homogeneous redistribution of hydrogen over measurement times.

Φ was calibrated as a function of $C_{H,diff}$ independently determined by electrochemical extraction [6]. UHSS samples were prepared and H pre-charged potentiostatically as described previously at H overpotentials (η_H) ranging from –150 mV to –1000 mV (–982 to –1832 mV_{SCE}) with a Pt mesh counter electrode [23]. Electrochemical H extraction was accomplished within 5 minutes, with less than 10% H loss. For extraction, a 60 min potentiostatic hold was applied at η_H of +330 mV (–649 mV_{SCE}) in 0.1 M NaOH, pH 12.5 solution, well above the reversible H Nernst potential ($E_{r, H+/H}$), to oxidize dissolved diffusible H [6]. $C_{H,diff}$ was determined from the H oxidation current at 1800 s, corrected for the background current density of an uncharged sample, using $D_{H,eff}$

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values of 3.1 and 6.2×10^{-9} cm²/s for the as annealed/CT and H900 temper, respectively [33]. A second calibration for Φ vs. $C_{H,diff}$ in UNS K92580 a non-stainless UHSS (Fe–10.89Ni–2.78Cr–1.21Mo–0.23C–0.019Mn (wt%)) was conducted for comparison [34].

For measurement of Φ versus $C_{H,diff}$, UNS S46500 steel was similarly pre-charged potentiostatically. Post-charging, samples were prepared in the same manner and within 5 min were inserted into a KP Technology Ambient Advanced SKP with a 50 μ m gold coated stainless steel tip for measurement, and calibrated to an Au/Al standard. Line scans, averaging 15 min to acquire, were taken from the uncharged zone of the sample, across the center of the pre-charged zone, and back to the uncharged zone. The distance between the SKP tip and the sample surface was controlled by a fixed gradient between the sample and probe tip with an average height of 5–10 μ m. Line scans over 14,986 μ m were taken in 57% RH ambient lab air (0.016 atm H₂O, 0.2 atm O₂, 0.78 atm N₂) with 3 measurements averaged per point and a step size of 254 μ m (initial measurement taken at 0) [1]. Steels were compared in uncharged and pre-charged conditions. The average Φ from pre-charged areas of the steel was correlated with $C_{H,diff}$ at each charging overpotential, η_H .

1.2. SKP of pitted samples

UNS S46500 H900 was prepared in the same manner. A 10 μ L, 7000 μ m average diameter, droplet of 3.9 M MgCl₂ (the equilibrium salt concentration) was deposited, and the sample was exposed for 2 weeks to ambient lab air at room temperature, at 58% RH set by saturated NaBr solution [35]. Pits developed, ≈ 40 μ m in diameter, in each droplet within the first 24 h of exposure. Only one dominant pit formed per droplet.

Corrosion products at pits on well-passivated samples were removed mechanically and cleaned in the same manner as prior to SKP measurement. Initial line scans were taken in 57% RH ambient lab air across the area exposed under the droplet and near the pit, but not taken directly above the pit as to avoid influence of topography on Φ . After the line scan, an area scan was acquired over the area occupied by the droplet. The area scan required 4 hours and only provided a qualitative image of the H uptake spatially as some H outgassing and redistribution (e.g., 10 μ m diffusion length) may occur over this time frame. Post area scan, a second line scan was taken for comparison.

A cross-section method was employed to determine the H distribution perpendicular to the corroded surface. UNS S46500 H900 was prepared and exposed in the same manner. The sample was cleaned and a 1 mm thick section (Fig. 1) was taken near the pit. The time between removal of the sample from the exposure and SKP measurement was 15 min. An area scan, 19 mm² with step size of 31.8 μ m was taken along the surface from which the pit initiated with depth into the sample, Fig. 1-b. Since the section was taken proximate to, but parallel to the

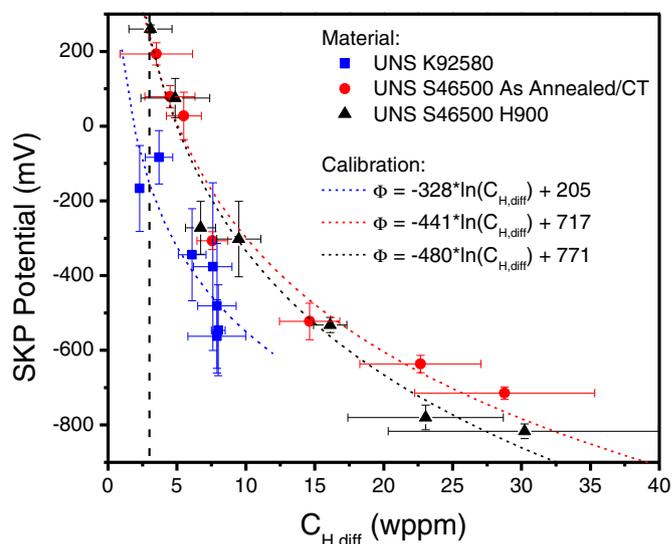


Fig. 2. a) $C_{H,diff}$ vs Φ in 57% RH (0.16 kPa H₂O, 20.26 kPa O₂, 79.03 kPa N₂ and 0.55 kPa residual gas species) ambient air for as annealed/CT and H900 temper UNS S46500 and UNS K92580, with error bars showing the standard deviation.

depth axis of the pit, Φ measured in the area scan is not influenced by sample topography. An unexposed sample was cross-sectioned and compared.

2. Results and discussion

2.1. SKP calibration

The average Φ vs. the η_H can be combined with the measurements of $C_{H,diff}$ vs. η_H to create a calibration curve giving the relationship between $C_{H,diff}$ and Φ (Fig. 2). The Φ decreases with increasing $C_{H,diff}$ in both steels. A lower range of $C_{H,diff}$ was achieved in UNS K92580 as expected, at the same range of η_H [36].

2.2. SKP of pitted steels

The SKP line scan at 15 min shows a more negative Φ at the periphery of the pit on the pre-exposed UHSS, indicative of the locally enhanced $C_{H,diff}$ (Fig. 3-a). While the exact concentration at the pit bottom is uncertain, speculatively, it is 10 wppm given a Φ of -300 mV [17]. The second line scan, taken 4 h post-exposure, displays a rise in Φ , specifically above the pre-charged areas, indicative of H degassing and redistributing with time. An SKP area scan shows a similar trend in Φ ; however, it is an indication of the H levels achieved, as significant

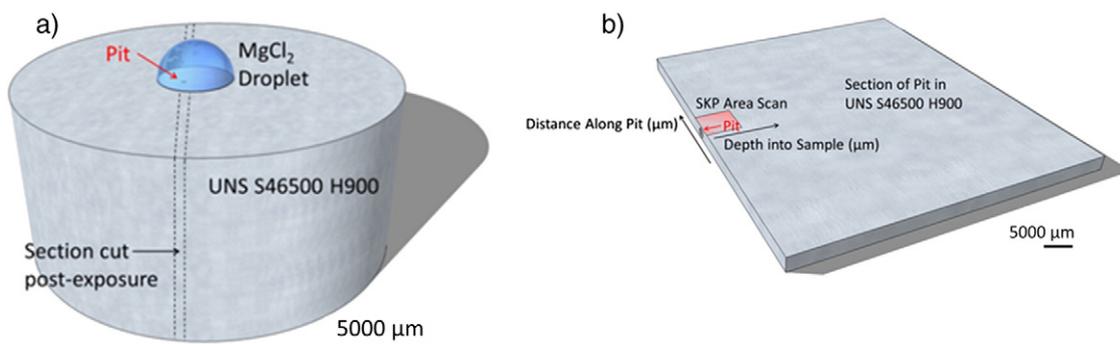


Fig. 1. Schematic of a) droplet pre-exposure with location of cross-sectional cut and b) cross-sectional surface utilized for an SKP scan shown on section taken around pit after exposure.

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