# Identification of Hydrogen Uptake Sites and Local Hydrogen Concentrations During Atmospheric Exposure of Steels Using Scanning Kelvin Probe Microscopy and Electrochemical Extraction

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Ultra high strength steels (UHSS) are attractive for many high performance applications, particularly under high stresses. Many UHSS are low alloy steels that historically require coatings to control general corrosion. Recently, interest has progressed away from heavy metal coatings on alloys to designing alloys with intrinsic corrosion resistance in an effort to eliminate environmentally hazardous heavy metals. [1] However, most martensitic, age-hardenable stainless alloys exhibit a much lower resistance to localized corrosion than conventional stainless steels. Consequently, under deliquescing salt deposits, they may go acid-based pitting, enabling local hydrogen production and uptake. [2] In contrast, low alloy steels may form traditional Evans type cells which experience local H uptake at spatially distributed anode sites such as drop interiors. Either circumstance can lead to H environment assisted cracking (HEAC), which is a strong function of H concentration, $C_H$ in both UHSS.[3, 4] While much has been reported on the effect and quantification of H uptake under full immersion conditions with and without cathodic protection, [4-6] little data exists for atmospheric exposures. [7, 8]

This presentation explores the effect of relative humidity (RH) under atmospheric exposure conditions on H production and uptake. Both the chloride concentration and droplet size of deposited aerosols are controlled by the RH. [9] Two distinct H producing corrosion cells may form during atmospheric H ingress; H production and uptake in an Evans drop and/or local uptake in pits. [10, 11] Details of $Cl^-$ concentrations, relative electrochemical local potential, and resulting pH in droplets govern atmospheric corrosion and thus H production and uptake.
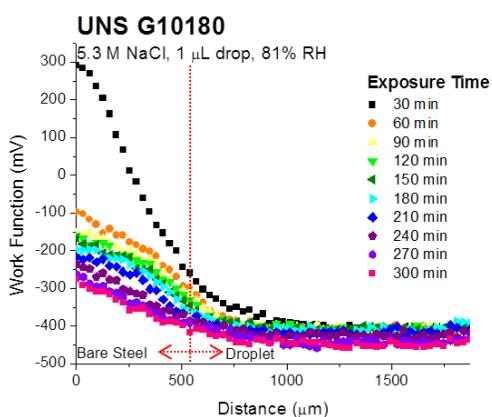


**Figure 1.** SKP work function measurement across a 5.3 M NaCl droplet at 81% RH on UNS G10180.

Three ferrous alloys were investigated here; martensitic, secondary age hardened UNS K92580 (Fe-3Cr-11Ni-13Co-1.2Mo; wt. %) and UNS S46500 (Fe-12Cr-11Ni-1Mo-2Ti; wt%), and as a control, UNS G10180 (Fe-0.18C-0.6Mn; wt. %). Micropipetted droplets were investigated in a Scanning Kelvin Probe (SKP) microscope with a controlled RH chamber. Stable droplets, of various sizes (0.2 - 2μL) and concentrations (0.9- 5.3 M NaCl and $MgCl_2$), were deposited on steel samples, exposed at the selected equilibrium RH for a corresponding salt concentration, and mapped by the SKP to obtain local work function and potential (Figure 1). Using SKP, Rohwerder et. al.[12] have shown that interstitial H affects the work function of a metal. However, here, the primary factor is the effect of $Cl^-$ on electrochemical potential under a droplet due to Evans drop or passivity breakdown and pit formation. [13, 14] Its subsequent effect on H uptake is evaluated using a database of electrochemical extraction data for H uptake in full immersion environments.

SKP mapping, along with pH measurements taken for the exposed droplets using Universal pH Indicator, enabled H overpotential mapping for specific pH. The local spatial distribution of the diffusible H concentration ($C_{H, diff}$) across a droplet under atmospheric exposure was predicted from this. Post-exposure corrosion morphologies (Evans Drop vs. pitting) were analyzed through profilometry. Corrosion products were characterized by scanning electron microscopy and X-ray diffraction.

The comparison of SKP potential mapping to electrochemical extraction measurements of $C_{H,diff}$ enabled understanding of the potent H uptake sites and local scale H concentrations. Corrosion analysis gave insight into the effects of material composition on corrosion morphology, in terms of pitting/ general corrosion, and how this influences H uptake under these atmospheric conditions. A comparison of the effects of droplet salt concentration and size versus H uptake, and further studies of material compositions and resultant corrosion rates are presented here.

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